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SPECIAL TOPIC — New generation solar cells

Effect of hydroxyl on dye-sensitized solar cells assembled with TiO_2 nanorods

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TiO_2 nanorods have been prepared on ITO substrates by dc reactive magnetron sputtering technique. The hydroxyl groups have been introduced on the nanorods surface. The structure and the optical properties of these nanorods have been studied. The dye-sensitized solar cells (DSSCs) have been assembled using these TiO_2 nanorods as photoelectrode. And the effect of the hydroxyl groups on the properties of the photoelectric conversion of the DSSCs has been studied.

Keywords: hydroxyl groups, TiO_2 nanorod, dye-sensitized solar cells, sputtering

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1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted significant attention due to their special features, such as low cost and high light to electricity conversion efficiency. The cells generally are composed by a dye adsorbed nanoporous material, typically TiO_2, and an electrolyte solution as a hole transport layer containing a dissolved iodide ion/tri-iodide ion redox couples.[1] The dye molecules absorb light to generate excited electron–hole pairs. The electrons are then injected into the porous TiO_2 photoelectrode and propagate through it until they are collected and transferred to the external electric circuit. The electron transport, recombination, and collection processes are three very important processes in DSSC and have been extensive studied.[2–18] In order to improve the conversion efficiency, the charge recombination possibility must be reduced. Therefore a high efficiency and fast charge transportation process is required. One dimensional (1D) nanostructures, such as nanorod, nanotube, and nanowire, show a promising solution to improve the charge transportation process. Electron transport in 1D structure is expected to be several orders of magnitude faster than that in random 3D nanostructure.[12,19,20] Many works have been done for 1D structure based DSSC and the conversation efficiency is approaching that for 3D nanoparticles based DSSC.[21–28]

Traditionally, the photoelectrodes of DSSC are made by a chemical method which needs a high temperature (450 °C) treatment for the densification of the TiO_2 films. This high temperature treatment will cause a problem for producing the flexible cells as the polymeric substrates could not endure such a high temperature. Magnetron sputtering technique has been considered as industrial processes that are applicable to large scale deposition with high uniformity at a relatively low deposition temperature. In the beginning of this century, some works on DSSC using TiO_2 electrode prepared by sputtering technique have been reported by Goméz *et al.*[29,30] Recently, some other groups have also reported the results on DSSC based on TiO_2 films prepared by sputtering technique.[31–34] So far, the energy conversion efficiency is still low for the DSSCs based on sputtered TiO_2 films as they cannot adsorb a large amount of dye molecules because of the lower specific surface area resulting from the compact structure which is a typical characteristic of the sputtered films. In our previous work, the TiO_2 nanorods have been made by dc reactive magnetron sputtering and the effects of the nanorods dimension, blocking layer, and annealing temperature on the efficiency of DSSCs have been reported.[35–39] It is well known that the ability to adsorb photosensitive dyes can be improved by introducing the surface hydroxyl groups. In this work, the effect of the surface hydroxyl groups on the structure of the nanorods is discussed and the DSSCs are assembled using these TiO_2 nanorods as the electrode. The photovoltaic properties of the DSSCs are studied.

2. Experimental section

The titanium oxide nanorods were deposited both on glass and commercial ITO substrates by dc reactive magnetron sputtering technique. The nanorods deposited on glass substrates were used for the simulations of the transmittance for obtain-

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ing the film thickness and the optical constants. The nanorods deposited on ITO substrates were used for dye-sensitized solar cells. The resistance of the ITO substrate is 30–40 Ω per square. The titanium metal with a purity of 99.99% ($\Phi 60 \times 3$ mm, Grikin Advanced Materials Co. Ltd.) was used as the sputtering target. The vacuum chamber was pumped using a turbo molecular pump backed with a mechanic pump. Before the deposition, the chamber was pumped down to 1×10^{-3} Pa, and then high purity Ar and O_2 gases were introduced into the chamber through the individual mass flow controller. The oxygen partial pressure and the total sputtering pressure in the chamber were kept at 0.3 Pa and 1.5 Pa, respectively for all deposition processes. The target–substrate distance was kept at 60 mm. No extra heating and biasing was applied to the substrate during all the deposition processes. The sputtering current and the cathode potential were kept at 0.5 A and 400 V, respectively for all the depositions. The deposition time was 6 hours. The hydroxyl group was introduced by passing the oxygen gas through water before it was introduced into the chamber. The water was kept at the room temperature before it was introduced into the chamber. We did not measure the temperature of the water after it was introduced into the chamber. It is suggested that the temperature would be increased due to the effect of the plasma in the chamber. The sample prepared by this method was designated as the sample prepared with water and the sample prepared by normal condition was designated as the sample prepared without water.

The transmittance of the films was measured using a Jasco V-550 UV–Vis spectrophotometer. The film thickness and the optical constants were calculated by fitting the transmittance using Scout software. The x-ray diffraction (XRD) measurements were carried out using a Rigaku miniflex goniometer (30 kV, 15 mA). The surface morphologies were studied using field emission scanning electron microscope (FE-SEM). In order to get the clear images, the low vacuum model has been used. X-ray photoelectron spectroscopy (XPS) was recorded on a Thermo Escalab 250 equipped with a monochromatic Al $K\alpha$ x-ray source. The spectra were analyzed using CasaXPS (Casa Software, Ltd.). A standard Shirley baseline without any offset was used for background correction. The C 1s spectrum for adventitious carbon (284.8 eV) was used for charge correction. The deposited TiO_2 films were sensitized with N719 dye by soaking the films in an ethanolic solution of the N719 dye (0.5 mM of $(Ru(II)L_2(NCS)_2$:2TBA, where L = 2,2'-bipyridyl-4,4'-dicarboxylic acid) for 24 hours at room temperature. The counter-electrode is sputtered Pt on the FTO glass and the electrolyte is composed of 0.1 M I_2, 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 1.5G (100 mW·cm^{-2}) illumination, and a water filter. The light intensity was adjusted to 100 mW/cm^2. The cells were tested using a metal mask with an active area of 0.15 cm^2.

3. Results and discussion

In order to see the formation of the hydroxyl group in the sample surface, the detailed XPS spectra of O 1s and Ti 2p for TiO_2 nanorods prepared with and without water have been measured as shown in Fig. 1. The O 1s peak can be deconvoluted by three peaks located at 529.8 eV, 531.6 eV, and 533.2 eV respectively. The strongest peak located at 529.8 eV can be attributed to O–Ti bonding (O^{2-}), while the other two peaks located at the higher energy side (531.6 eV and 533.2 eV) can be attributed to the hydroxyl groups (OH^-) and hydrate and/or adsorbed water (H_2O). It can be seen that the intensity of the peaks related with the OH groups is much higher for the sample prepared with water than that for the sample prepared without water. It can be suggested that the hydroxyl groups have been formed by introducing the water during the sputtering process and result in a high OH group peak intensity. For Ti 2p, two peaks located at 458.2 eV and 463.8 eV are detected, which correspond to Ti $2p_{3/2}$ and $2p_{1/2}$, respectively. The samples prepared with and without water show similar Ti 2p spectra. It indicates that the introducing of the hydroxyl groups does not affect the Ti 2p spectra.

SEM images of the TiO_2 nanorods prepared with and without water are shown in Fig. 2. It can be seen that the samples prepared with and without water have a similar nanorod structure. The increase of the surface hydroxyl group does not affect the TiO_2 nanorod structure.

Figure 3 shows the XRD patterns of TiO_2 nanorods prepared with and without water. All the peaks in the XRD patterns can be indexed as the anatase phase of TiO_2 and the diffraction data are in good agreement with PDF card 21–1272. No other phase of TiO_2 is observed. It can be seen that the TiO_2 nanorods prepared with and without water have a preferred orientation along the [110] direction. However, the TiO_2 nanorods prepared with water have a stronger (220) diffraction peak intensity than that prepared without water. The intensity of the (101) diffraction peak is similar for the two samples. The (101) and the (220) peak intensities have been calculated by fitting the XRD patterns and the ratio $I(220)/I(101)$ for the nanorods prepared with and without water has been obtained. The ratio is 61 and 24 for the nanorods prepared with and without water, respectively. From Fig. 3, it can be seen that the (101) peak intensity does not have a very clear change for the samples prepared with and without water. It means that the preferred orientation along the [110] direction is enhanced for the TiO_2 nanorods prepared with water.

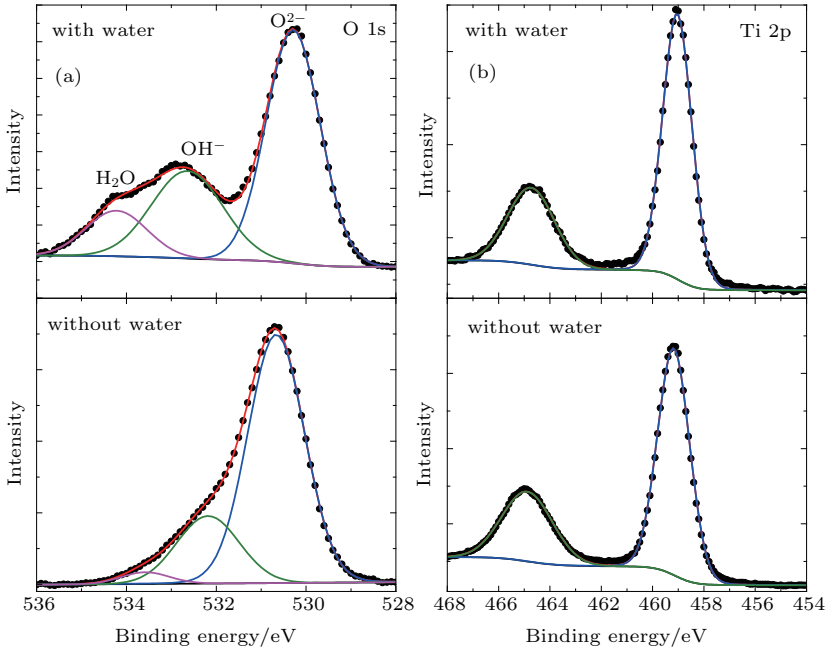


Fig. 1. (color online) High-resolution XPS spectra for the (a) O 1s and (b) Ti 2p peaks and respective fitting of the TiO_2 nanorods prepared with and without water.

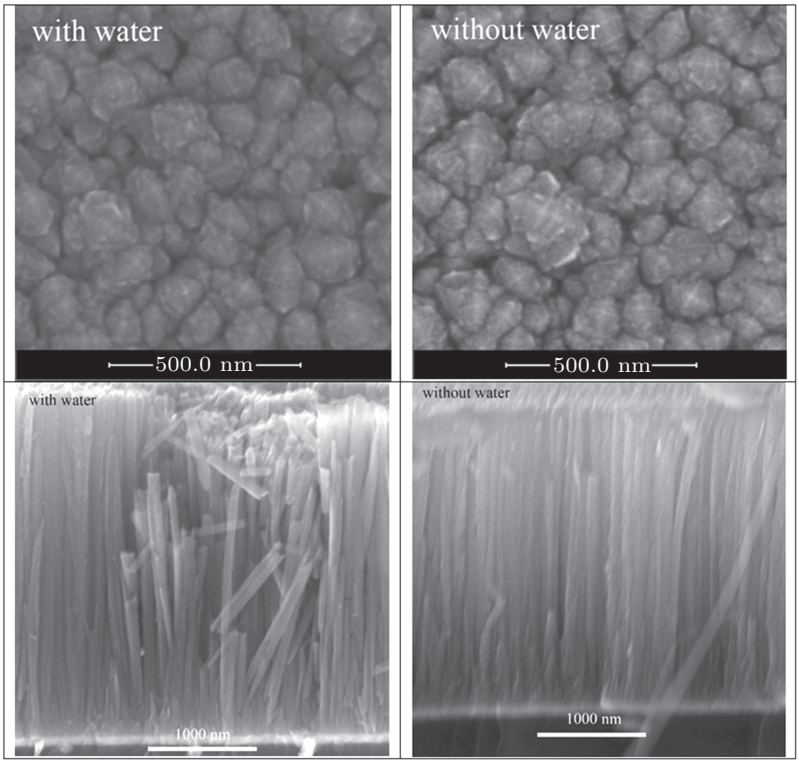


Fig. 2. (color online) The SEM images of TiO_2 nanorods prepared with and without water.

The average surface energies of the crystal planes of the anatase TiO_2 are related to the percentages of the 5-foldcoordinated titanium atoms on the specific planes and are 1.09 J/m^2, 0.90 J/m^2, 0.53 J/m^2, and 0.44 J/m^2 for the [110], [001], [100], and [101] crystal planes, respectively.[40] Usually, the [101] planes dominate anatase TiO_2 single crystal, which are thermodynamically stable due to a low surface energy. However, both the surface energy and the strain energy of grains formed in the films will affect the development of the texture for the polycrystalline films. The effects of strain energy minimization are qualitatively similar to those of surface and interface energy minimization in that normal grain growth can not occur until the subpopulation of grains favored by strain energy minimization has consumed all grains with other orientations.[41] The competition between surface energy and strain energy during film growth might contribute to

the changes in texture of the grains as observed in Fig. 3. For sufficiently thin films, surface and interface energy minimizing textures are favored; but for the thicker films with higher elastic strains, strain energy minimizing textures are formed.[41] It means that the (110) texture is dominated by strain energy minimization and the (101) texture is dominated by surface energy minimization in the growth process. By introducing water during the sputtering process, the mobility of the adatoms in the substrate might be low, which results in favorable strain energy minimizing textures during grain growth and a high (220) diffraction peak intensity.

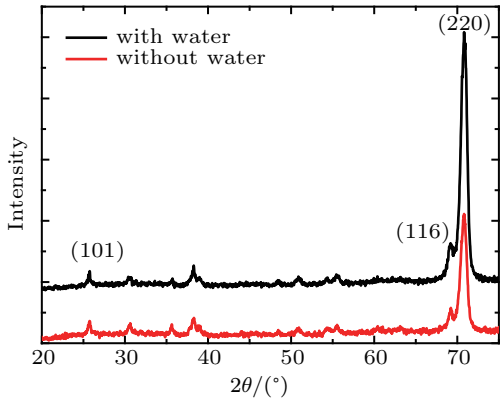


Fig. 3. (color online) The x-ray diffraction patterns of TiO_2 nanorods deposited onto ITO substrates with and without water.

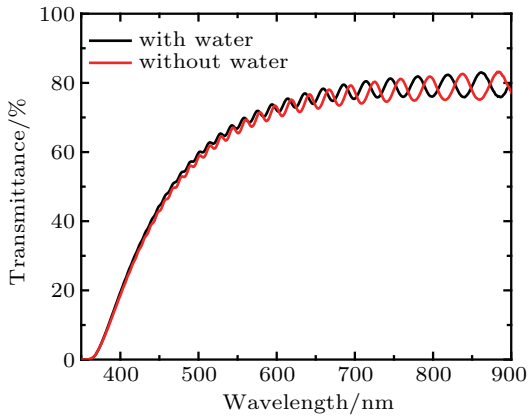


Fig. 4. (color online) The transmittance of the TiO_2 nanorods deposited on glass substrate with and without water.

Figure 4 shows the specular transmittance spectra of the TiO_2 nanorods prepared with and without water. The transmittance of the nanorods prepared with water is slightly higher than that of the nanorods prepared without water. By fitting the transmittance, the dispersion of the refractive index can be extracted. The results are shown in Fig. 5. The nanorods prepared without water have a higher refractive index than that prepared with water. The refractive index is related with the packing density of the sample. The hydroxyl groups in the sample surface may result in a decrease of the packing density and a low refractive index.

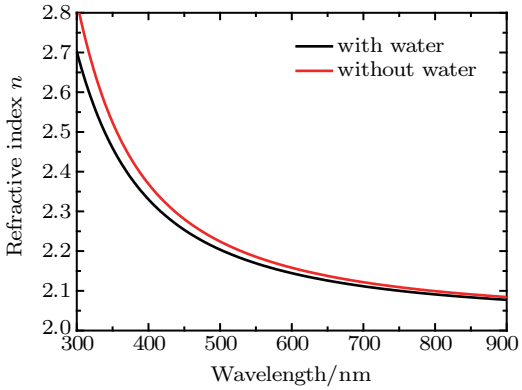


Fig. 5. (color online) The refractive index of the TiO_2 nanorods prepared with and without water.

Figure 6 shows the absorption spectra of the TiO_2 nanorods prepared with and without water. It can be seen that the dye absorption (around 500 nm wavelength) is much higher for TiO_2 nanorods prepared with water than that prepared without water. Although the specific surface area is not measured, the morphology and the dimension of the nanorods are very similar for the samples prepared with and without water as shown in Fig. 2. It means that the specific surface area does not change with the introduction of the hydroxyl groups. Therefore, the increase of the dye absorption results from the formation of the hydroxyl groups on the surface of the nanorods. The J–V curves of DSSCs using TiO_2 nanorods prepared with and without water as photoelectrode are plotted in Fig. 7 and the operation parameters are summarized in Table 1. The photoelectric conversion efficiency is calculated using the equation

$$\eta = \frac{J_{sc} V_{oc} FF}{P_{in}} \times 100\%,$$

where η is the conversion efficiency, J_{sc} is the short circuit current density which depends on the charge injection and transportation, V_{oc} is the open circuit voltage which is most likely related with the difference between the Fermi level of the semiconductor electrode and the redox potential in the electrolyte, FF is the fill factor which is related to functioning of the TiO_2/electrolyte interface, the higher the recombination of conduction band electrons with the electrolyte, the lower FF will be,[12] and P_{in} is the incident light energy. It can be seen clearly that the solar cell assembled with TiO_2 nanorods prepared with water has a higher photocurrent density comparing to that prepared without water. The presence of the hydroxyl groups increases the absorption of the dye molecular and results in a high photocurrent. However, a negative effect is also introduced by the hydroxyl groups on the nanorod surface. As it can be seen from Table 1 that the fill factor is lower for the solar cell assembled with nanorods prepared with water, which may reduce the conversion efficiency. It is no yet very clear why the introduction of the hydroxyl reduces the fill

factor. It is suggested that the introduction of the hydroxyl will modify the parasitic resistances of the cell and result in a low fill factor. The conversion efficiency is dominated by the photocurrent. By introducing the hydroxyl groups on the nanorods surface, the efficiency is increased from 3.1% to 3.8%.

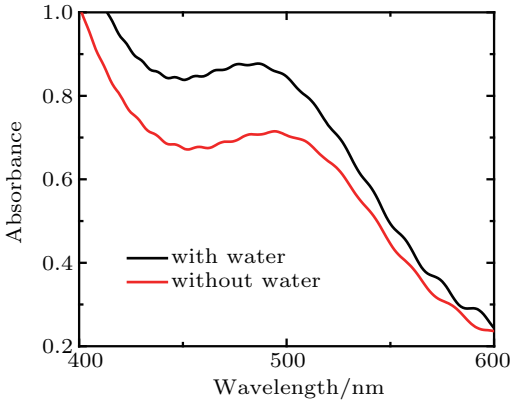


Fig. 6. (color online) Absorption spectra of TiO_2 nanorods prepared with and without water after dye sensitized.

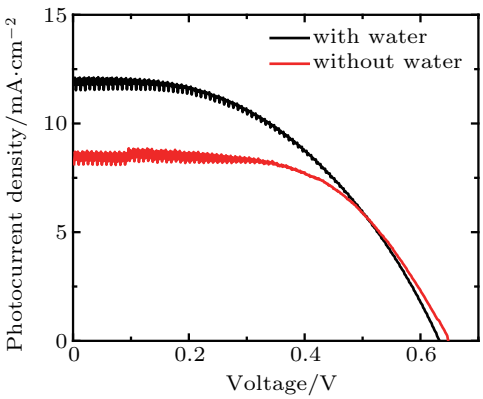


Fig. 7. (color online) Current-potential characteristics of the TiO_2 nanorods prepared with and without water.

Table 1. Performance comparison of the DSSCs assembled with TiO_2 nanorods prepared with and without water.

	J_{sc}/mA·cm^{-2}	V_{oc}/V	FF	η/%
Without water	8.4	0.64	0.58	3.1
With water	12.1	0.63	0.50	3.8

4. Conclusion

TiO_2 nanorods were prepared by dc reactive magnetron sputtering. The hydroxyl groups on the nanorod surface were introduced by passing the oxygen reactive gas through water. The preferred orientation along the [110] direction has been enhanced and the dye absorption has been improved by the hydroxyl groups. The DSSCs assembled using TiO_2 nanorods with hydroxyl groups show a better conversion efficiency than those using TiO_2 nanorods without hydroxyl groups.

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