

Fabrication of highly efficient dye-sensitized solar cell and CO₂ reduction photocatalyst using TiO₂ nanoparticles prepared by spin coating-assisted sol-gel method

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Abstract A sol-gel method was applied for fabrication of nanocrystalline anatase TiO₂ thin films on ITO glass substrates and followed by rapid thermal annealing for application as the work electrode for dye-sensitized solar cells (DSSC). TiO₂ nanoparticles were characterized by X-ray diffraction (XRD) pattern and scanning electron microscopy (SEM) and the absorption of dye on the TiO₂ electrode was shown by UV-vis spectroscopy. By controlling different parameters including numbers of coated layers, the gap between two electrodes, sensitization time, and light source power, TiO₂-based solar cells with high efficiency was achieved. The results show that a five time spin-coated TiO₂ electrode with applying sealant and sensitization time of 24 h in N3 dye under illumination of 100 W cm⁻² tungsten lamp give the optimum power conversion efficiency (η) of 6.61%. The increases in thickness of TiO₂ films by increasing the numbers of coated layers can improve adsorption of the N3 dye

through TiO₂ layers to increase the open-circuit voltage (V_{oc}). However, short-circuit photocurrents (J_{sc}) of DSSCs with a one-coated layer of TiO₂ films are smaller than those of DSSCs with five-coated layer of TiO₂ films. It could be due to the fact that the increased thickness of TiO₂ thin films also resulted in a decrease in the transmittance of TiO₂ thin films. Also, this electrode was employed to photoreduce CO₂ with H₂O under tungsten lamp as light source.

Keywords Dye-sensitized solar cell (DSSC) · TiO₂ nanoparticles · Photocatalytic redox reaction · Spin coating · Sol-gel

Introduction

Dye-sensitized solar cells (DSSCs) have been the subject of intense study on account of their high conversion efficiency, low cost, less toxic manufacturing, easy scale-up, light weight, and use of flexible panels compared to conventional p-n junction devices. In the conventional p-n junction solar cells, only the electrons and holes which can diffuse to the space charge region can be collected as a current. To get a long diffusion length, the purity of semiconductors should be increased and the defect concentration should be decreased, resulting in the expensive solar cell materials. In a DSSC, a photon absorbed by a dye molecule gives rise to electron injection into the conduction band of nanocrystalline oxide semiconductors. Because of the high surface area, relatively high photocurrent can be obtained in spite of the simple process [1–5].

The optoelectronic functional materials with a high response to UV and visible light have been pursued in the last several decades. Titanium dioxide (TiO₂) as an n-type

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wide band gap semiconductor is one of the most promising candidates among them. However, this material is only sensitive to UV light due to its large band gap (3.1 or 3.2 eV), along with a relatively high electron–hole recombination rate. All these impede its application in many fields, such as photocatalysis and photovoltaic. By designing proper electrode thickness and sensitization dyes, TiO₂ DSSCs are able to absorb most of the light [6–8].

The techniques for the film processing should be developed in the view of both aspects of favorable economy and ecology, to make the technique applicable for the increasing demand in the future. Although many sophisticated techniques, namely, vacuum evaporation [9], sputtering [10], chemical vapor deposition [11], molecular beam epitaxy [12], etc. are being used. These techniques are energy-intensive and involve high temperature. Researchers also studied wet chemical processes from the economic considerations and some other advantages such as simplicity and low temperature processing. One of the wet chemical processes is spin coating-assisted sol–gel which is inexpensive and easily adaptable to industry scale and mass production [13]. It is possible to work in normal atmospheric conditions and get high homogeneity of the final coatings. The process can be controlled by temperature or through the chemical contents and their molar ratios.

The operation of the DSSC is closely related to the nanometer scale morphology of the TiO₂ electrode and the molecular nature of the dye–TiO₂–electrolyte interface. To achieve higher efficiency of DSSC, it is necessary to increase the efficiency of electron transport in TiO₂ mesoporous film to decrease electron recombination losses [14–16]. One process that limits the efficiency of the DSSC is the re-capture of the injected electron by the oxidized mediator before the electron has been collected and passed through the load and counter electrode. The highest reported laboratory scale efficiency in a DSSC is 10.4% obtained with the black dye [17]. Good stability of over thousands of hours has been reported in light soaking experiments for the cells using the N3 dye [cis-Ru(dcbpy)₂(NCS)₂ where dcbpy is 4,4′-dicarboxylic acid-2,2′-bipyridine] or Ru535 [18].

Photocatalytic CO₂ reduction using sunlight that resembles natural photosynthesis is a direct method to both decrease greenhouse gas and supply sustainable energy to us. Although this concept seems to simply solve the serious issue of energy shortage, too low efficiency of the process requires much more studies to bring it to practical applications. Owing to the successful stories of DSSC as previously mentioned, reduction of CO₂ over Ruthenium dye-sensitized TiO₂-based catalysts in an optical-fiber photoreactor was investigated by Wu [19] and The-Vinh and Jeffrey [20].

In this research, a typical DSSC was made using sol–gel and spin coating method. The efficiency of the solar cell

was considered by Ru535 sensitized TiO₂. In this method, polyethylene glycol was applied for creating more porosity for increasing dye absorption of TiO₂ semiconductor. Also, the cell was applied in the photocatalytic reaction of CO₂.

Experimental

Materials

All the chemical reagents used in our experiments were of analytical grade and were used as received without further purification. Isopropanol, H₂PtCl₆, EtOH, titanium tetraisopropoxide (TTIP), HCl, acetonitrile, I₂, LiI, butanol and polyethylene glycol (PEG, MW = 1,500) as sealant were purchased from Merck and used as received. 4-tert-butylpyridine (TBP) was purchased from Aldrich and Ru535 (N3) was obtained from Solaronix.

Characterization

The characterization of samples was performed using scanning electron micrograph (SEM) (model XL30 made in Netherlands) with 20 kV increment and at least 4 mm operation, to determine the morphology of samples. XRD measurements were done with diffractometer Bruker, D8DVANCE, Germany using Cu K_α radiation in the scanning angle (2θ) range of 0–80. UV–vis absorbance spectra were recorded on double beam scanning spectrophotometer (SHIMADZU UV-2550) which equipped with a 1-cm path length glass cell. UV–vis spectrophotometer attached to a Pentium 400 MHz computer.

The photocurrent–voltage (I–V) curves were measured using a source measure unit under irradiation of white light from a 100 W Tungsten lamp (Thermo Oriel Instruments). The incident light was 1,000 mW cm^{−2}. The I–V curves were used to calculate the short-circuit current (J_{sc}), open-circuit voltage (V_{oc}), fill factor [a measure of the “squareness” of the solar cell (FF)], and overall conversion efficiency (η) of DSSC.

Fabrication of the TiO₂ electrode

TiO₂ nanoparticles were produced by a sol–gel method. In a typical synthesis route, 0.12 mol EtOH was added to 0.49 mol HCl and 0.008 mol titanium tetraisopropoxide (TTIP) was added to above solution under constant magnetic stirring and aged for 1 h to gain a uniform gel. After a 10 min grinding process, an additional 0.0005 mol PEG 1500 was added to the above solution to increase the porosity of the film. The obtained gel was spin coated onto the cleaned indium tin oxide, ITO conductive glass (15 Ω cm^{−2} resistivity) at 3,000 rpm for 5 min.

The coating procedure was repeated 1–5 times. The deposited film was calcined at 500 °C for 1 h in air.

Producing the Pt electrode

5.0×10^{-3} M isopropanol solution was produced from H_2PtCl_6 . Then a few drops of the platinum solution were dripped on the ITO glass with dimensions of $2 \times 2 \text{ cm}^2$ and in order to the stabilization of platinum on the ITO glass it was placed an electric furnace about 1 h at 375 °C.

Fabrication of dye-sensitized solar cells (DSSCs)

The resulting film was immersed in an 3.0×10^{-4} M solution of N3 pigment in 1:1 butanol:acetonitrile as solvent for 24 h. Then it was rinsed with pure ethanol for removing water in the pores inside the TiO_2 nanocrystals. After the sensitization, UV–vis spectrum was taken from electrode in both conditions, before and after sensitization. The dye-adsorbed electrode was assembled into a sandwich-type cell with a counter electrode and a spacer in the middle for ease of electrolyte solution injection. For the preparation of counter electrodes, a few drops of 5 mM solution of H_2PtCl_6 in isopropanol were allowed to spread on ITO. The plates were air dried for 5 min and heated at 375 °C for 1 h. The Pt electrode was placed over the dye-adsorbed TiO_2 electrode, and the edges of the cell were sealed with a tiny thickness foil of polyethylene. The sealant was not applied for all of the solar cells to see the effect of this part on the performance of the DSSCs. The redox electrolyte consisted of 0.5 M LiI, 0.04 M I_2 , and 0.5 M 4-tert-butylpyridine in acetonitrile as a solvent. A drop of electrolyte solution was introduced into the cell.

Using the solar cell in the photoreduction of CO_2

Photocatalytic reaction was carried out by putting the as-prepared dye-sensitized TiO_2 electrode (with five TiO_2 -coated layers) in a Pyrex glass vessel (320 cm^3) placed in appropriate position to be directly irradiated by a light source (W lamp with a peak light intensity at 350 nm). The moisture CO_2 gas (1 atm) was passed through the vessel for 1 h after turning on the UV light. The reaction was continued for 4 h.

Results and discussion

Characteristics of the TiO_2 samples

The XRD diffraction pattern of the as-prepared sample was recorded for the identification of the product (Fig. 1a). It confirms that the product is titanium dioxide. All

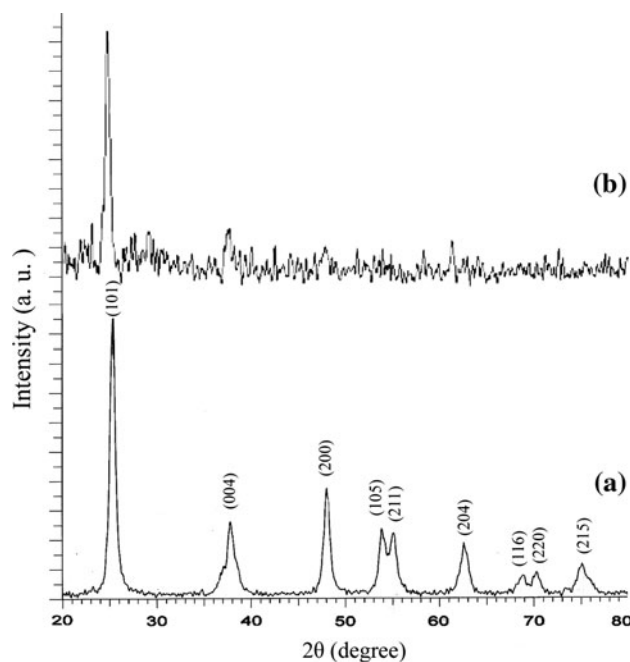


Fig. 1 The XRD patterns of **a** TiO_2 nanoparticles powder, **b** TiO_2 nanoparticles as film electrode calcined at 500 °C

diffraction peaks can be indexed to the pure anatase TiO_2 crystalline phase. The crystallite size diameter (D) of the TiO_2 nanoparticles has been calculated by Debye–Scherrer equation ($D = 0.9\lambda/\beta\cos\theta$) [21] where β -FWHM (full-width at half-maximum, or half-width) is in radians, θ is the position of the maximum of diffraction peak and λ is the X-ray wavelength (1.5406 \AA for Cu $K\alpha$). Crystallite size of initial powder has been found to be about 10 nm.

The red lines shown in the XRD spectrum resulting from TiO_2 nanoparticles is in good agreement with the standard spectrum of TiO_2 particles [16]. Also, XRD was used to investigate the changes of phase structures and crystallite sizes of the TiO_2 nanoparticles after spreading on the ITO and calcination at 500 °C. Figure 1b shows the XRD pattern of the film electrode. It can be observed that the crystallinity of TiO_2 nanoparticles is quantitatively evaluated via the relative intensity of the (101) diffraction peak of the anatase [22] but there are several small peaks and noises found in the spectrum, corresponding to glass substrate. In this case, the size of the sintered TiO_2 nanoparticles is calculated to be about 12 nm and it is also in good agreement with standard TiO_2 nanoparticles.

Figure 2a shows the SEM images of TiO_2 nanoparticles synthesized by spin coating mediated sol–gel method. The average diameter of the particles calculated from the micrograph gives the value close to 55 nm which this large value is probably due to the agglomeration of small nanoparticles. This image shows the formation of a three-dimensional network with typical spherical structures that

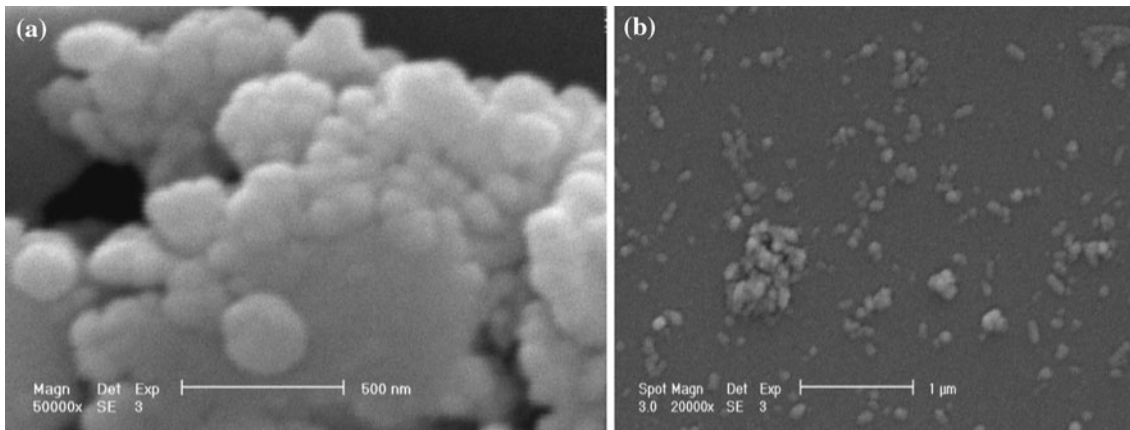


Fig. 2 SEM micrographs of nanostructured TiO_2 synthesized by spin coating-assisted sol-gel method for **a** five TiO_2 blocking layers and **b** five TiO_2 blocking absorption dye

are tightly linked together. Figure 2b shows SEM micrographs of nanostructured TiO_2 for five TiO_2 blocking dye absorption. After sensitization of the nanoparticles by dye, the uniform distribution was occurred and it indicates that the dye absorption on the TiO_2 electrode leads to increase the efficiency of the photocell [16]. The mean size of the nanoparticles on the TiO_2 electrode was about 70–120 nm.

Absorbing N3 dye on TiO_2 electrode

To ensure that dye is absorbed on the surface of TiO_2 film electrode, UV-vis spectrometry was performed on the samples. Figure 3 shows the variation of UV-vis transmittance of percentage pigment. Figure 4 shows the variation of UV-vis transmittance of both bare and dye-coated TiO_2 film on ITO surface (TiO_2 coated for 5 times) with the wavelength of the incident radiation in the range of 300–600 nm. The decreased transparency of the dye-sensitized film determines relatively high absorption once the TiO_2 layer is dye-sensitized. It is obvious from Fig. 4b that there is higher transmittance in the ultraviolet region due to its transmittance from the TiO_2 nanoparticles rather than the dye molecules whereas the absorption in the visible

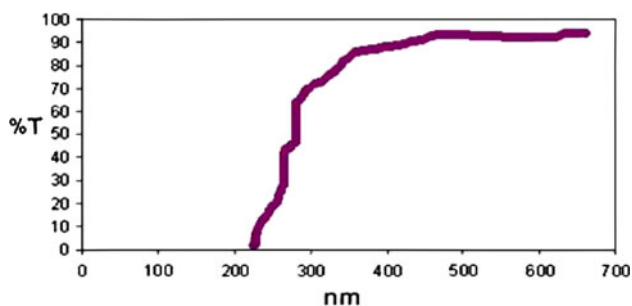


Fig. 3 UV-vis transmittance spectra of percentage pigment

region is attributed to the absorption by dye molecules [23].

Photovoltaic performance

The performance of fabricated solar cells has been tested under the same condition and some important parameters in the procedure have been studied which are discussed as follows:

Effect of the number of coated layers

By repeating the deposition procedure, the performance of the fabricated solar cells with different TiO_2 -coated layers was examined. Table 1 shows the various parameters of DSSC with different coated layers. As the number of blocking layers was increased from 1 to either 3 or 5, the open-circuit voltage increased. It is likely that the first layer does not completely cover the substrate and still contains some small holes. When further layers are coated, the film

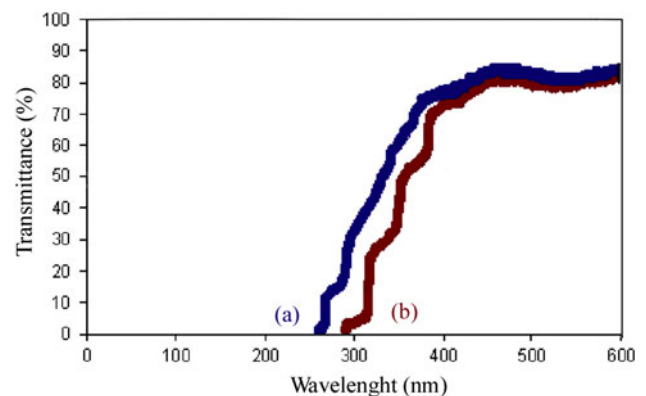


Fig. 4 UV-vis transmittance spectra of **a** bare TiO_2 and **b** $\text{TiO}_2/\text{N3}$ dye substrates

becomes smooth and uniform and the holes are filled and leads to complete coverage of the substrate. This increases the uniformity and smoothness of the compact TiO₂ films and probably also contributes to the improvement of solar cell performance when the number of blocking layers will be increased. The increasing of the efficiency, η , was largely due to an increasing of short-circuit current, J_{sc} , resulting from the prevention of the back transfer of electrons from the conducting layer on the glass substrate to the electrolyte. As the number of coatings increases, the efficiency of the solar cells also increases because of providing better coverage of the substrate due to the compact TiO₂ and increasing of the film and thus providing a greater barrier to the back transfer of electrons [11, 12]. Figures 5 and 6 both show the I–V curve for DSSC with different numbers of TiO₂-coated layers (1 and 5) under illumination of two different light sources. It can be observed that V_{oc} and η increase with the increase of the TiO₂-coated film. It is due to the larger film thickness of TiO₂ thin film that results in a higher adsorption of the N3 dye through the TiO₂ layers. However, the J_{sc} and η of DSSC with one number of TiO₂-coated film are smaller than those of DSSC with five number of TiO₂-coated layers. This can be explained by the lower transmittance of the thicker TiO₂ thin film to reduce the incident light intensity on the N3 dye. Kao et al. [24] have deposited nanocrystalline anatase TiO₂ thin films with different thicknesses (0.5–2.0 μm) on ITO-coated glass substrates by a similar spin coating-assisted sol–gel method used in this work. They obtained the optimum power conversion efficiency of 2.9% in a DSSC with the TiO₂ film thickness of 1.5 μm . In our work, the optimum η of 6.61% with J_{sc} and V_{oc} of 9.1 mA/cm² and 1.067 V, respectively, was obtained by the five number of TiO₂-coated layer film under illumination of 100 W/cm² tungsten light source. These results may be illustrated by decreasing the gap energy of TiO₂ affected by the N3 dye

compared to the other dyes especially N886 and N719 [25, 26].

Effect of applying sealant

Sealant or foam layer used here is a tiny thickness foil of polyethylene glycol to prevent the evaporation of the electrolyte. Using the sealant between two electrodes prevents the rapid evaporation of existing acetonitrile in the electrolyte and increases the duration of electric current in solar cell circuit, thus it promotes the efficiency of the cell. The results of using sealant in the DSSC are shown in Table 1. By comparing cells No. 3 and 6, the values of 4.50 and 6.61 are obtained for efficiency of the cell, respectively. Also, cells No. 9 and 12 have been compared and the efficiencies of 4.11 and 5.36 have been calculated, respectively. All these data show that how effective is the sealant in improving the efficiency of solar cells.

Effect of sensitization time

A requirement for the dye structure is that it should possess several O or –OH groups capable of anchoring to the Ti(IV) sites on the TiO₂ surface. The molecular structure of N3 dye exhibits the O and OH groups, which are responsible for the transferring of excited electrons into TiO₂. The following processes may describe the dye sensitization into TiO₂: (1) diffusion of dye into TiO₂ nanostructured, (2) adsorption of the dye to the TiO₂ surface, and (3) dissolution of Ti surface atoms from TiO₂ and formation of Ti²⁺/dye complex in the pores of the TiO₂ film. Depending upon the rate of these different processes, the outer part of the electrode form Ti²⁺/dye complexes in the pores, when dye molecules reach the interface between the bulk contact and the TiO₂ film. Therefore, the latter process increases the efficiency,

Table 1 The Photovoltaic properties of solar cells with no sealant (foam or blocking layer) and with one, three and five compact TiO₂ sol–gel blocking layers with tungsten and xenon lamps

Cell no.	Using sealant	Irradiation source	Sensitization time	Number of TiO ₂ layer	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF	% η
1	No	Tung	24 h	1	10	0.331	54.0 (54)	4.00 (4.8)
2	No	Tung	24 h	3	9.8	0.506	52.9 (51)	4.29 (5)
3	No	Tung	24 h	5	9.6	0.608	51.7 (52)	4.50 (5.49)
4	No	Tung	10 day	3	9.5	0.531	53.0	4.31
5	No	Tung	10 day	5	9.3	0.620	52.0	4.54
6	Yes	Tung	24 h	5	9.1	1.067	69.0	6.61
7	No	Xe	24 h	1	8.4	0.291	54.0	3.62
8	No	Xe	24 h	3	8.34	0.495	52.3	3.85
9	No	Xe	24 h	5	8.31	0.585	51.0	4.11
10	No	Xe	10 day	3	8.29	0.509	52.8	3.54
11	No	Xe	10 day	5	8.25	0.607	51.8	4.00
12	Yes	Xe	24 h	5	8.2	0.923	50.0	5.36

whereas the former is responsible for the decrease in the efficiency [27]. Here, the effect of sensitization time in the dye solution on the performance of DSSC was studied. Two different times, 24 h and 10 days, were chosen. By comparing cells No. 2 and 4 or cells No. 9 and 11, it can be concluded that increasing the sensitization time of TiO₂ electrode by N3 dye has a small effect on V_{oc} and FF. The efficiencies of cells No. 2 and 4 are 4.29 and 4.31, and for cells No. 9 and 11 are 4.11 and 5.36, respectively. It shows that the prolongation of the sensitization time increases the efficiency. We propose that in contrast with ZnO DSSCs [28], in the case of TiO₂ the pH of the dye solution is similar to the ZnO DSSC [29] so Ti²⁺/dye complex is not formed easily. Therefore, by prolonging the sensitization time, more dye molecules reach the interface between the bulk contact and the TiO₂ film while a few numbers of TiO₂ dissolve to form Ti²⁺/dye complex. This is why higher efficiencies are observed by increasing sensitization time (Table 1).

The effect of light source

As was mentioned above, Figs. 4 and 5 show the I–V curve for DSSC with different light sources (400 W Xenon lamp and 100 W tungsten lamp). By comparing these two figures and the data in Table 1, it can be seen that under illumination of tungsten lamp, for solar cells with different numbers of TiO₂-coated layers, the J_{sc} , V_{oc} , FF and η increase. At low light intensity a balance is established between J_{sc} and V_{oc} values and the solar cells with five-coated layer exhibit the highest overall conversion efficiency (6.61%). This can be a consequence of a modest variation in the photocurrent density compared to the change in the V_{oc} values. In other words, at low light intensity, fewer electrons are photogenerated and the demand for a highly conductive medium to compensate for dye cation regeneration is not crucial [30].

Using the solar cell in the photoreduction of CO₂

Because of the hydrophilic photocatalytic property of the electrode and for prevention of decreasing of the electrode surface due to electron transfer between the electronic levels of TiO₂ nanoparticles in the presence of H₂O molecules [20], the photocatalytic reaction of CO₂ with H₂O was considered in the gas phase by the solar cell with five TiO₂-coated layers under illumination of tungsten lamp. To make comparison between operation of the electrode before and after photocatalytic reaction, the electrode was used in fabrication of solar cell. The voltage, power and fill factor parameters of the electrode were compared with those measured with the electrode before photocatalytic reaction. The results are listed in Table 2.

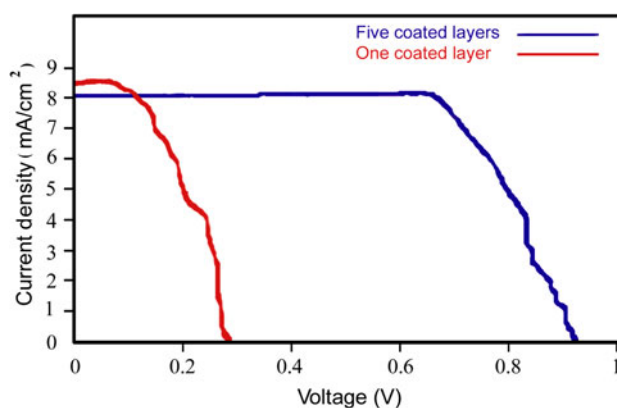


Fig. 5 I–V curve for DSSC with one (Cell No. 7) and five (Cell No. 12) TiO₂-coated layers under 400 mW cm⁻² xenon light irradiation

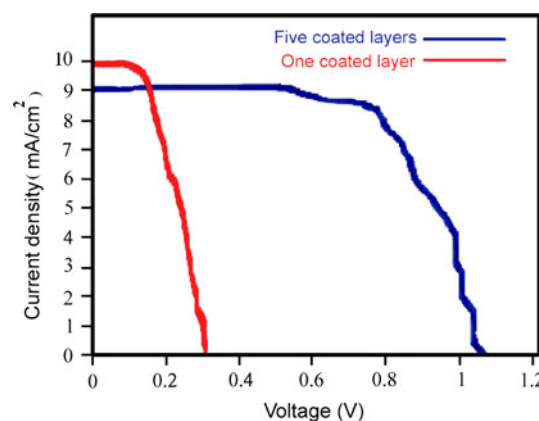


Fig. 6 I–V curve for DSSC with one (Cell No. 1) and five (Cell No. 6) TiO₂-coated layers under 100 mW cm⁻² tungsten light irradiation

Table 2 The values of photovoltaic properties of the solar cell with five TiO₂-coated layers under illumination of tungsten lamp before (a) and after (b) the photocatalytic redox reaction of CO₂ and H₂O

Open-circuit voltage (V)	Fill-factor (RSD%)	% η (RSD%)
(a) 1.067	69 (± 0.2)	6.61 (± 0.2)
(b) 0.502	86 (± 0.9)	3.88 (± 0.2)

RSD values are calculated for two entries

Conclusions

The TiO₂ nanoparticles were made by the sol–gel method and the ITO glass was deposited in the spin coating of the as-prepared nanoparticles. The influence of different parameters including number of coated layers, the gap between two electrodes, sensitization time, and light source power on the performance of DSSC with TiO₂ films was studied. With increasing the spin-coated layer of TiO₂ from 1 to 5 under illumination of tungsten lamp and xenon lamp, the values of V_{oc} of DSSC increased from 0.331 to 1.067 V

and from 0.291 to 0.923 V, respectively. However, the J_{sc} of DSSCs with five times TiO_2 spin coating under tungsten and xenon lamp (8.2 and 9.1 mA/cm²) is smaller than those of DSSC with one spin-coated layer (8.4 and 10 mA/cm²), respectively. This can be explained by the lower incident light intensity from the lower transmittance of the thicker TiO_2 film. The corresponding results show that the obtained DSSC with the five time spin-coated TiO_2 thin film exhibited excellent photovoltaic properties. Finally, the TiO_2 electrode was applied in the photocatalytic redox reaction of CO_2 and H_2O . The application of this method in large scale will promise the development of cheap solar cells in the future.

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