REVIEW

Preparation of nanocrystalline TiO$_2$ thin film at low temperature and its application in dye-sensitized solar cell

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Abstract The electrophoretic deposition combined with common pressure hydrothermal treatment was employed to prepare nanocrystalline TiO$_2$ thin film from suspension of tetra-*n*-butyl titanate and P25 at low temperature. The tetra-*n*-butyl titanate was hydrolyzed and crystallized into anatase to interconnect nanocrystalline TiO$_2$ particles and to stick them to a conductive substrate by common pressure hydrothermal treatment to improve the electron transport properties of the deposited thin film. A dye-sensitized solar cell based on TiO$_2$ thin film prepared by the low temperature method yielded the conversion efficiency of 6.12%. Due to the relative slower electron transport rate in the deposited film, its conversion efficiency was slightly lower than that of the cell with TiO$_2$ thin film prepared by the conventional high temperature sintering method. Since it is free of high temperature sintering step, this method can be used to prepare nanocrystalline TiO$_2$ thin film on plastic polymer conductive substrate for fabrication of flexible dye-sensitized solar cell.

Keywords Electrophoretic deposition · Nanocrystalline TiO$_2$ thin film · Common pressure hydrothermal treatment · Low temperature preparation · Dye-sensitized solar cell

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Introduction

Since the pioneer work of Regan and Gratzel was reported in 1991 [1], technologies of dye-sensitized solar cells (DSSCs) have stimulated a number of studies on efficiency and stability improvements of DSSCs. To realize a commercially competitive technology of DSSCs, it is imperative to employ a technique to prepare nanocrystalline thin film on flexible organic substrate, aiming at increasing the flexibility and reducing the weight as well as the overall device thickness of DSSCs. The key operation of glass-to-plastic substrates conversion is to prepare mesoporous TiO$_2$ thin film at low temperature with a high surface area for dye adsorption and a high degree of crystallinity for fast transport of electrons. Several methods to prepare semiconductor thin films on flexible substrates have been reported, such as the low temperature annealing at ~100 °C and the compressing method at the pressure of ~2,000 kg cm^{-2} [2–5]. In addition, low temperature processes for preparing nanoporous thin films on conducting glass or flexible substrate have been intensively studied by means of electrophoretic deposition [6–8], chemical deposition [9–11], binder-free coating, hydrothermal synthesis, etc. [12, 13].

However, such thin films prepared by the low temperature method were found to have a larger inherent resistance than that prepared by the conventional high temperature sintering method that was demonstrated by electrochemical impedance spectroscopy [14]. Time- and frequency-resolved photoelectrochemical measurements showed that the diffusion coefficient and the lifetime of electrons in such thin films are not comparable with that in the films prepared by the high temperature sintering method, resulting in lower photocurrent, fill factor, and conversion efficiency of DSSCs [15, 16]. Therefore, in order to improve the performance of DSSCs, it is necessary

to strengthen the inter-particles connectivity and the adherence of the film to a conducting substrate at low temperature. According to the literature, the films prepared by the low temperature methods were post-treated by microwave irradiation [6] and UV light-assisted chemical vapor deposition (CVD) of TiO$_2$ [17, 18] to reinforce inter-particle binding of TiO$_2$, which is indispensable to ensure photoelectric activity. There are also some other methods to improve the properties of films by making different kinds of modifications [19–21].

Recently, we have firstly brought in a new preparation method of nanostructured TiO$_2$ thin film at low temperature via a hydrothermal reaction at the solid/liquid interface [22]. The common pressure hydrothermal method is a simple low temperature preparation method and is convenient and cheap compared to high temperature sintering. The hydrothermal reaction can take place in a non-sealed system at 100 °C at common pressure. The prepared TiO$_2$ thin films are porous and mechanically stable even without the high temperature sintering process. The most important thing is that the flexible polymer substrates can be used favorably in this way. Furthermore, it is also beneficial to the preparation of large scale cells and mass production.

In this study, the method of electrophoretic deposition combined with common pressure hydrothermal treatment was employed to prepare nanocrystalline porous TiO$_2$ thin film, which was used as photoelectrode to fabricate DSSC. A satisfactory performance of DSSC prepared by our low temperature method was presented, and the effect of the common pressure hydrothermal treatment on the improvement of properties of the deposited TiO$_2$ thin film was discussed.

Experimental

All chemicals used were of analytical reagent grade without further purification. The fluorine-doped tin oxide transparent conductive glass (FTO, 20 Ω/sq, Hake New Energy Co., Ltd. Harbin) was ultrasonically cleaned sequentially in detergent solution, acetone, and finally in Milli-Q pure water.

Nanocrystalline TiO$_2$ powder (Degussa P25, 30% rutile and 70% anatase; particle size, 25 nm; BET surface area, 55 m^2 g^{-1}) of 0.5 g and tetra-*n*-butyl titanate (TBT) of 0.034 g were added to a mixture of 8 mL butanol, 4 mL *iso*-propanol, and 2 mL ethanol, followed by magnetic stirring for 2 h to obtain TiO$_2$ colloid solution with appropriate viscosity for electrophoretic deposition. To prepare the porous TiO$_2$ thin film, electrophoretic deposition was carried out as follows: two pieces of FTO were immersed face to face into the TiO$_2$ suspension and applied by a DC field of 48 V cm^{-1} for 30 s. TiO$_2$ particles with surface positive charge diffuse to a negative electrode and are deposited on FTO to form porous TiO$_2$ thin film under the

applied DC field. The as-deposited TiO$_2$ thin film was rinsed with TBT butanol solution (0.2 mol L^{-1}) and dried in an oven at 40 °C for 2 h. Then, the TiO$_2$ thin film was heat-treated in a non-sealed container full of water (common pressure hydrothermal process) or in an oven at 100 °C for 4 h. Heating treatment of TiO$_2$ thin film at 100 °C was carried out to evaluate the effect of common pressure hydrothermal process. To compare the conversion efficiency of DSSCs based on the TiO$_2$ thin film electrode prepared at high and low temperatures, the deposited film was also subjected to a sintering treatment at 450 °C for 30 min.

Dye sensitization was performed by immersing the TiO$_2$ thin film electrode into 5×10^{-4} mol L^{-1} ethanol solution of Ru(dcbpy)$_2$(NCS)$_2$ (dcbpy: 2,2′-bipyridine4, 4′-dicarboxylic acid) (N3, Solaronix) for 12 h at room temperature. The dye-sensitized thin film was used as the working electrode and platinum foils as counter electrode to assemble sandwich DSSC. The electrolyte was 0.5 mol L^{-1} LiI (Aldrich), 0.05 mol L^{-1} I$_2$ (Aldrich), and 0.5 mol L^{-1} 4-*tert*-butylpyridine (Aldrich) in 3-methoxypropionitrile. Current–voltage (I–V) curves of the cells were measured with Potentiostat/Galvanostat Model 273 (EG&G) under light intensity of 100 mW cm^{-2} at AM 1.5 offered by a solar light simulator (Oriel, 91160-1000), and the active cell area was 0.2 cm^2. The intensity of incident light was calibrated with a radiant power/energy meter (Oriel, 70260) before each measurement.

The surface morphology of TiO$_2$ thin film was observed by a scanning electron microscope (SEM, Hitachi S-4300, 15 kV). The effect of common pressure hydrothermal treatment on crystallization and phase-purity of amorphous TiO$_2$ was investigated by measuring X-ray diffraction patterns (XRD) of the hydrolysis product of TBT treated by employing the common pressure hydrothermal process on a Rigaku D/max 2500 using Cu Kα irradiation.

In measuring the intensity-modulated photocurrent spectroscopy (IMPS) response of DSSC, high-intensity blue LEDs (470 nm), which led to a DC light intensity of up to 2.0 mW cm^{-2} at the electrodes, were used as light sources. The light intensities were modulated by the sine voltage applied to the LED under the frequency range of 0.1 Hz to 10 kHz. The amplitude and phase shift of the current response with respect to the modulation of the light intensity were measured with the Solartron 1255B frequency response analyzer (FRA) and Solartron SI 1287 electrochemical interface system. The control of FRA and data acquisition during measurements was carried out using a personal computer.

Results and discussion

Electrophoretic deposition of TiO$_2$ nanoparticles has been studied under a higher applied electric field, such as

1,200 V cm^{-1} [6–8]. In contrast to the reported method, in our case, a lower electric field of 48 V cm^{-1} was applied to deposit P25 TiO$_2$ particles on FTO substrate by electrophoresis. After 30 s of electrophoretic deposition, an opaque TiO$_2$ thin film with the thickness of 8 μm was homogeneously deposited on the surface of conductive FTO glass. The surface morphology of the as-deposited film was shown in SEM image (Fig. 1a). Particles are piled up to form TiO$_2$ thin film. Owing to the easy aggregation of TiO$_2$ particles in the as-deposited film, a uniform porous structure was not observed. Moreover, the mechanical strength of the film is so weak that the film sheds from the glass substrate easily. It is the physical force under electric field that connects P25 nanoparticles to each other during the electrophoretic deposition. As the physically adsorbed force between particles in the film far from the FTO substrate is not strong enough, the TiO$_2$ thin film based on these particles with bad contact will have an opposite effect on the energy conversion efficiency of

DSSC. Therefore, after electrophoretic deposition, the treatment to glue these loose particles becomes necessary.

In our experiment, the as-deposited film was rinsed in 0.2 mol L^{-1} TBT butanol solution to connect these loose P25 nanoparticles by hydrolyzing TBT into TiO$_2$. Then, the hydrolyzed amorphous TiO$_2$ was crystallized by the common pressure hydrothermal treatment of the deposited film following our reported original method [22]. TBT wash combined with common pressure hydrothermal treatment, hereafter named as the water-cooked treatment, acts like adding a "glue" to connect TiO$_2$ particles as well as to attach the film to the substrate, thus forming a film with high mechanical stability. The surface morphology of the film treated by the water-cooked process was observed by SEM and shown in Fig. 1b. It shows that small hydrolyzed TiO$_2$ particles existed in the as-deposited film. The newly formed TiO$_2$ among P25 particles act as the joints in a net to link those loose particles, consequently, improving the particle connection as well as the contact of the thin film with the conductive FTO substrate. In short, the application of the water-cooked treatment not only can wash off badly connected particles, but also can improve the connection of the remaining particles resulting in a film with good particle connection.

In this work, TiO$_2$ thin films prepared from mixed pastes of TBT and P25 have the advantages of good mechanical stability and non-solubility in water, ethanol, and electrolyte, which are the benefits derived from using the water-cooked treatment. During the treatment, the TiO$_2$ thin film electrode is completely immersed in water with the temperature of 100 °C, leading to the hydrothermal crystallization reaction at the solid/liquid interface. To prove the crystallization of hydrolyzed TiO$_2$ during the water-cooked process, XRD patterns of the TiO$_2$ films prepared by spreading the solutions of TBT on FTO glass substrates with different post treatment were measured and shown in Fig. 2. The TiO$_2$ film does not exhibit crystalline characteristics after heating in air at 100 °C for 4 h, illustrating that TBT was hydrolyzed into amorphous TiO$_2$. However, when the film was put into water to carry out the water-cooked treatment at 100 °C for 4 h, the hydrolyzed TiO$_2$ of TBT can be crystallized into anatase. This crystallization could reduce the defects and surface states of the film and increase its electron transport rate.

As the high temperature sintering step is omitted in the above procedure, it is a convenient way to prepare the nanocrystalline TiO$_2$ thin film photoelectrode on flexible conductive substrate for fabrication of flexible DSSCs. The electrophoretic deposited nanoporous TiO$_2$ electrodes treated by the water-cooked method at 100 °C or heated in air at 100 °C were sensitized with Ru(dcbpy)$_2$(NCS)$_2$ for fabrication of DSSCs to analyze the effect of the water-cooked treatment. Figure 3 showed the typical photocurrent–
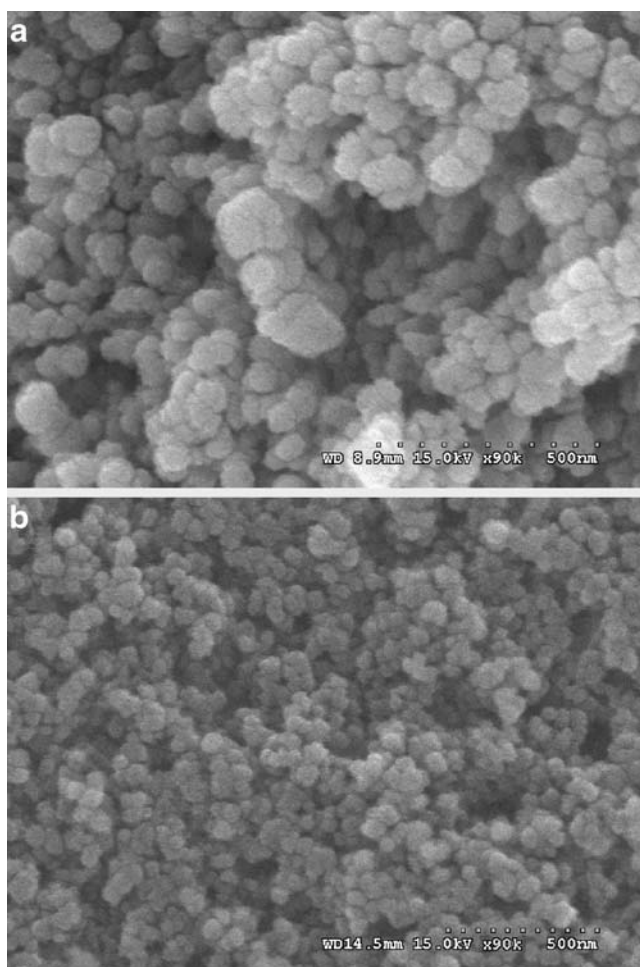

Fig. 1 SEM images of the electrophoretic deposited TiO$_2$ thin films. **a** The as-deposited film; (**b**) the film treated by water-cooked method
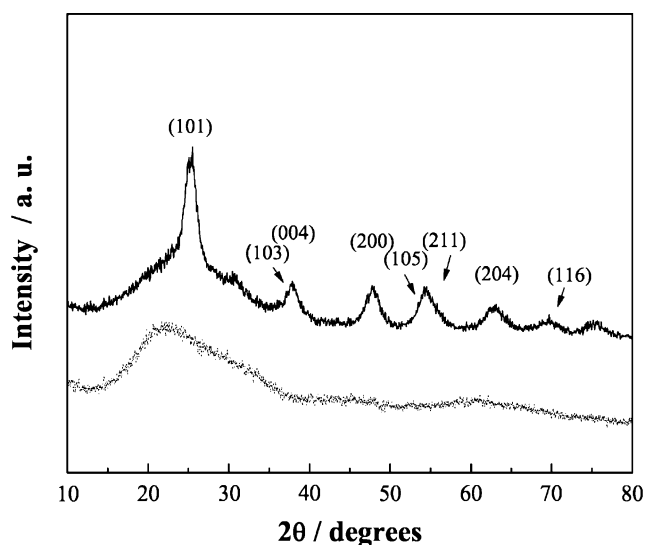
Fig. 2 XRD patterns of TBT hydrolysis treated by heating in air at 100 °C for 4 h (*dash line*) or water-cooked treatment at 100 °C for 4 h (*solid line*)

voltage curves of the above two cells, and their performance parameters were compared in Table 1. The short circuit photocurrent (J_{SC}) and conversion efficiency of DSSC based on the deposited film using the water-cooked treatment are higher than that heated in air. Their dye loading amounts listed in Table 1 are similar, indicating that the enhancement of conversion efficiency for the cell based on water-cooked treatment is not due to the increase in surface area or porosity of the film. Also, the film thickness was also found unchanged after the water-cooked treatment.
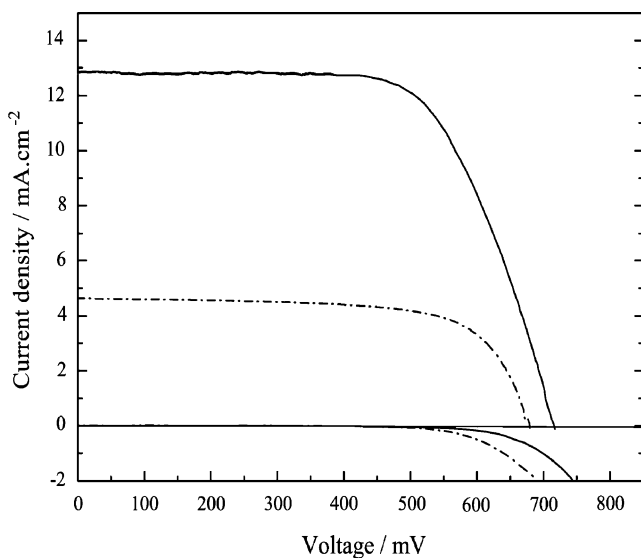
Table 1 Sensitized properties of the electrophoretic deposited films

	J_{SC}/ mA cm^{-2}	V_{OC}/ mV	Conversion efficiency/%	ff	Dye loading/ mol cm^{-2}
100 °C heated	4.59	682	2.22	0.71	0.59×10^{-7}
100 °C water-cooked	12.85	715	6.12	0.68	0.62×10^{-7}
450 °C sintered	14.6	686	6.20	0.62	0.89×10^{-7}

The transport process of photoinjected electrons in the TiO$_2$ thin film could be studied by measuring their IMPS response under short circuit conditions. Typical complex plane plots of IMPS response of DSSCs based on deposited films with and without water-cooked treatment were illustrated in Fig. 4. The IMPS response is characterized by a semicircle in the third and fourth quadrants of the complex plane corresponding to the RC and the diffusion controlled electron transport processes in nanocrystalline thin film. Electron transport time (τ_D) can be calculated directly from IMPS response by the following equation:

$$\tau_D = \frac{1}{\omega_{min}} = \frac{1}{2\pi f_{min}} \tag{1}$$

where ω_{min} is the angular frequency, and f_{min} is the frequency at the minimum of the semicircle in the IMPS plot. After the water-cooked treatment, IMPS response shifts towards higher frequencies, indicating that the electron transports faster in the water-cooked film (τ_D/ 1.59×10^{-2} s) than in the film heated at 100 °C for 4 h (τ_D/

Fig. 3 Current–voltage curves of DSSCs under illumination of AM 1.5 and in the dark. TiO$_2$ photoelectrode prepared by electrophoretic deposition with heating at 100 °C for 4 h (*dash dot line*) or with water-cooked treatment at 100 °C for 4 h (*solid line*), scanning rate is 25 mV s^{-1}
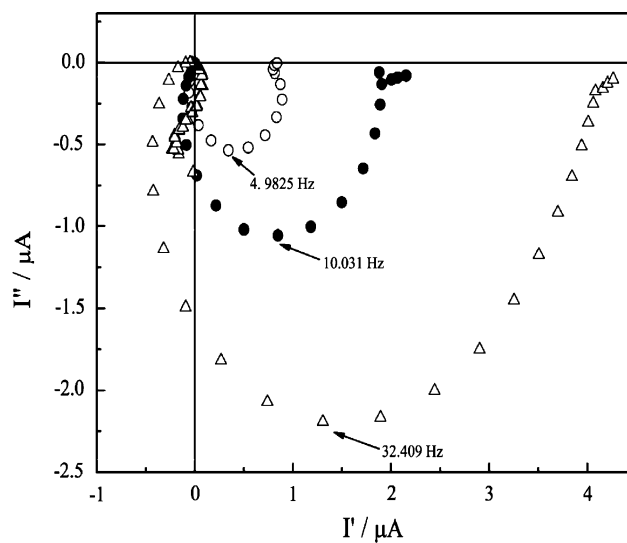

Fig. 4 IMPS plots for dye-sensitized TiO$_2$ thin films measured with an incident DC light intensity of 2.0 mW cm^{-2}. The deposited film treated by water-cooked method at 100 °C for 4 h (*filled circle*), heated in air at 100 °C for 4 h (*open circle*) or sintered at 450 °C for 30 min (*open triangle*)

3.2×10^{-2} s). As there are no significant differences in dye loading amounts and thicknesses of the two films, τ_D enables the comparison of electron transport properties. Therefore, the larger photocurrent obtained in the film that underwent the water-cooked treatment is attributed to its faster electron transport ability. As mentioned above, during the water-cooked treatment, the newly formed anatase TiO$_2$ not only can improve the connection between P25 particles, but also can reduce their surface defects. As a result, lower electron trap density and higher electron transport rate in the thin film are obtained.

Current–voltage curves of DSSCs based on the above two films were measured in the dark and shown in Fig. 3. The dark current is caused by the recombination of electrons in a semiconductor thin film with redox ions in electrolyte. The injected electrons in the film heated at 100 °C are more likely to be recombined than that in the film that underwent the water-cooked process. Furthermore, a larger dark current was observed for the film heated at 100 °C as shown in Fig. 3. TiO$_2$ hydrolyzed on the uncovered surface of FTO and surface states of P25 particles suppress the recombination of electron on conduction band with hole collector in the electrolyte, resulting in a higher voltage, and it is consistent with the open circuit photovoltage (V_{OC}) data listed in Table 1.

Summarizing the results of IMPS under illumination and I–V curve measurements in the dark, we can conclude that the hydrolyzed amorphous TiO$_2$ is crystallized into anatase, which form connection among particles during the water-cooked treatment. Crystals growing in inter-particles shorten electron transport time in the film and on the surface states suppress the recombination of electrons on the conduction band with redox electrolyte. Both of them improve the performance of DSSC based on the deposited thin film treated by the water-cooked process.

In comparison with the high temperature sintering method, the electrophoretic deposited TiO$_2$ thin film electrode washed by TBT butanol solution was sintered at 450 °C for 30 min or treated by water-cooked process to fabricate DSSCs. The performance of two cells based on high temperature sintering method and water-cooked treatment was shown in Fig. 5. The conversion efficiency of the cell fabricated by the film sintered at 450 °C is slightly higher than that prepared by the water-cooked method. One reason for lower efficiency of DSSC based on low temperature treatment may be the small amounts of amorphous TiO$_2$ that remained in the film after the water-cooked treatment, whereas high temperature sintering of the electrophoretic deposited TiO$_2$ film would lead to complete crystallization of TiO$_2$. As a result, the transport time of electron in the film sintered at high temperature obtained from IMPS ($\tau_D/4.9\times10^{-3}$ s) is faster than that in the film treated by the low temperature method as shown in Fig. 4.
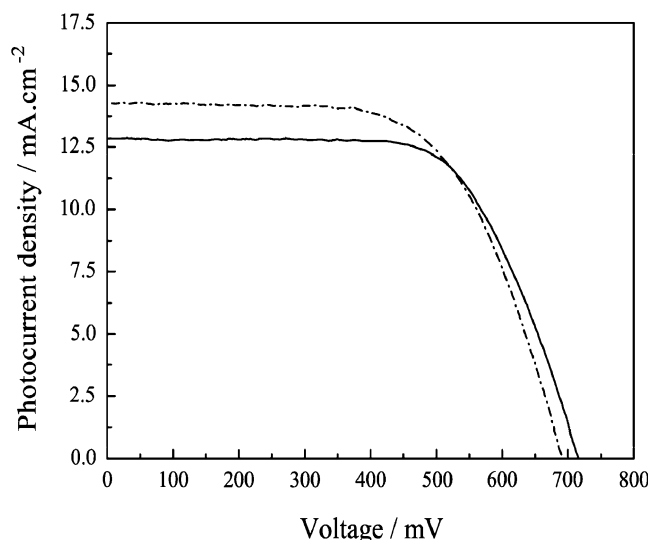

Fig. 5 Current–voltage curves of DSSCs under illumination of AM 1.5. The deposited TiO$_2$ thin film treated by water-cooked method at 100 °C for 4 h (*solid line*) or sintered at 450 °C for 30 min (*dash dot line*), scanning rate is 25 mV s^{-1}

In addition, the possible residual organics butanol and TBT are considered as a factor to limit the efficiency of DSSC prepared by the low temperature method. Namely, after hydrolyzation, some organic materials cannot be removed completely that may have a negative effect on the performance of DSSCs. With further treatment of UV–O$_3$ [23] or microwave irradiation [6], these organic materials may be removed completely. Although the electron transport rate and the efficiency are lower in the film prepared using our low temperature method than that fabricated by the sintering technique, this method can be used to prepare nanocrystalline TiO$_2$ thin film on a flexible conducting substrate.

Conclusions

The TiO$_2$ thin film electrode prepared by electrophoretic deposition combined with water-cooked treatment exhibited good mechanical stability and high photovoltaic performance. The cell with TiO$_2$ thin film that underwent water-cooked treatment after the electrophoretic deposition process yielded conversion efficiency of 6.12%. The higher light-to-electricity conversion efficiency is attributed to the improvement of particle connection and reduction of surface states due to hydrolysis of TBT followed by crystallization of amorphous TiO$_2$ during water-cooked treatment. The film based on the low temperature method shows slight lower conversion efficiency than that fabricated by the conventional high temperature sintering method due to its slower electron transport rate and larger inherent resistance. However, our low temperature method is

possible to be applied to the fabrication of flexible dye-sensitized solar cell for the sintering step is elided.

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