

# Chemical sintering of graded TiO<sub>2</sub> film at low-temperature for flexible dye-sensitized solar cells

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## Abstract

A mesoporous nanocrystalline graded TiO<sub>2</sub> film was prepared on either a transparent conductive glass (ITO/glass) or a transparent conductive polymer (ITO/PEN, PEN = poly(ethylene naphthalene-2,6-dicarboxylate) through a doctor-blade method and then treated by chemical sintering at 150 °C. The graded film, which has a large specific surface area, high porosity, and proper strength, was composed of particles with different sizes and appropriate ratios. The effects of the smallest particles for binding and the largest particles for light scattering were studied. High light-to-energy conversion efficiencies of 4.10% and 3.05% were obtained within the dye-sensitized solar cells (DSSCs) fabricated by using the graded films on ITO/glass and ITO/PEN, respectively. The results show that the graded structure has promising applications in DSSCs.

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**Keywords:** Graded structure; ITO/PEN; Doctor-blade; Low-temperature film preparation; Chemical sintering

## 1. Introduction

Dye-sensitized solar cells (DSSCs) were widely investigated due to their low production cost and potentially high conversion efficiency during the last decade [1,2]. A typical DSSC consists of a dye-sensitized nanoporous TiO<sub>2</sub> film on a transparent conductive glass (e.g., ITO glass) as a photoanode, a platinized conductive glass as a counter electrode, and a liquid electrolyte containing iodide/triiodide (I<sup>-</sup>/I<sub>3</sub><sup>-</sup>) redox couple. The TiO<sub>2</sub> film, which serves as the supporter of the dye molecules for light adsorption and electrons acceptor/transporter, requires a high-surface area, porosity, and good connections between TiO<sub>2</sub> nanoparticles. A high-surface area and porosity can allow a large quantity of dye to be adsorbed, which makes it possible to adsorb a large quantity of photons. Good connections such as necking and chemical bonds between TiO<sub>2</sub> particles, which are usually obtained by sintering the TiO<sub>2</sub> film at a temperature of 450 °C, are necessary to ensure the rapid electron transport in the TiO<sub>2</sub> film.

Flexible DSSCs based on a transparent conductive polymer have attracted a lot of interest because of their lightweight, flex-

ibility, and low cost in recent years. Because the heat treatment temperature for the polymer substrates are generally limited to a temperature lower than 150 °C, the preparation of nanoporous TiO<sub>2</sub> films with good connections between TiO<sub>2</sub> nanoparticles at temperatures less than 150 °C becomes a key issue. Generally speaking, low-temperature treatment would result in poor connections, which slow down the transport of photo-induced electrons in the film and give rise to electron recombination. What is more, the mechanical strength of the film treated at a low temperature is very poor. Several methods have been developed to prepare the nanocrystalline TiO<sub>2</sub> films at a low temperature, such as chemical deposition [3], mechanical press of nanocrystalline particles [4–7], hydrothermal necking [8,9], microwave sintering [10,11], and electrophoretic deposition [12,13]. Although good photovoltaic performance was obtained, all these methods required several steps, beginning with particle deposition and completing with interparticle connections. They are not suited for large-scale modules. Park et al. [14] have shown an easy way, by chemical sintering, to prepare low-temperature TiO<sub>2</sub> films in one step. Some viscous acid pastes were developed and deposited on transparent conductive polymers by the doctor-blade method followed by heat treatment at 150 °C. A conversion efficiency of 2.45% was obtained without scattering particles. This method makes the preparation of flexible DSSCs possible for industrial applications.

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In 2007, Miyasaka et al. reported a similar method to prepare nanocrystalline TiO<sub>2</sub> films at a low temperature [15,16]. Their TiO<sub>2</sub> films contained three different sizes of TiO<sub>2</sub> nanoparticles, which we named as the graded material in this paper. Graded material refers to a kind of structure where there are at least two kinds of particles with different sizes distributed in a special mode. In the system, smaller particles fill in the voids formed by the pileup of larger particles. Miyasaka et al. addressed the effects of particles size of the mean size TiO<sub>2</sub> particles, film thickness, and optimization of the electrolyte system. They obtained a high light-to-energy conversion efficiency of 5.8–6.4% under simulated sunlight of different intensities under optimized conditions.

However, they did not investigate the effects of the small particles for binding the mean size TiO<sub>2</sub> particles and the effects of the large particles for scattering. Moreover, they conducted the experiment without any theoretical calculation. In this paper, we focused on these two effects on such graded TiO<sub>2</sub> films by chemical sintering at a low temperature. First, a binary graded structure was designed by theoretical calculation, and then the effect of the ratio of different size particles on the photovoltaic properties of the DSSCs with such graded films was investigated. Photovoltaic properties of the DSSCs with the graded films both on transparent conductive glass (ITO/glass) and transparent conductive polymer (ITO/PEN, PEN = poly(ethylene naphthalene-2,6-dicarboxylate) were scrutinized. The connecting mechanism between TiO<sub>2</sub> nanoparticles in the graded film treated at a low temperature was also discussed.

## 2. Experimental

### 2.1. Preparation of the graded TiO<sub>2</sub> film and fabrication of DSSCs

Three types of particles with average diameters of 12, 28, and 100 nm were used in the present graded TiO<sub>2</sub> pastes. The particles with a diameter of 100 nm with pure anatase structure (Beijing Yili Chemical Company, China) were used as the scattering particles, referred to as the large particles. P25 particles (anatase:rutile = 7:3, Degussa, Germany) with an average diameter of 28 nm were accepted as the main part of the binary graded particles. The other part of the binary graded particles, TiO<sub>2</sub> nanoparticles with a diameter around 12 nm and referred to as the small particles, was prepared following the procedure as described in the literature [17]: hydrolyzing titanium tetraisobutoxide in the presence of nitric acid (pH 1), the hydrolysis slurry being heated to 80 °C and stirred vigorously for 8 h followed by autoclaving at 210 °C for 12 h. The resulting solution was named precursor 1.

P25 particles were mixed with precursor 1 in butanol, named paste 1. The large particles were mixed with P25 particles in the presence of butanol, named paste 2. Paste 3 was prepared by mixing paste 1 and paste 2 in appropriate ratios. There are two kinds of substrates used in the present study. One is ITO-coated glass (ITO/glass, sheet resistance of 8–10 Ω/□, Construction Materials Institute of Beijing, China), and the other is ITO-coated

polymer (ITO/PEN, 13–15 Ω/□, Tobi, Japan). The graded TiO<sub>2</sub> films were deposited with either paste 1 or paste 3 using the simple doctor-blade technique on the two kinds of substrates mentioned above, followed by heat treatment at 150 °C for 5 min. To study the effect of heat treatment, the graded films were also treated from room temperature to 450 °C. The thickness of the films heat-treated at 150 °C were about 3–4 μm, measured with a scanning electron microscopy (SEM, LEO 1530, Germany).

The graded TiO<sub>2</sub> films were immersed overnight in a dry ethanol solution of 5 mM ruthenium (2,2'-bipyridyl-4,4'-dicarboxylate)<sub>2</sub>(NCS)<sub>2</sub>(K-N719 dye, Kojima Chemicals Corporation, Japan) and then dried at room temperature to form photoanodes. One drop of an iodine-based electrolyte solution was deposited onto the surface of a dye-adsorbed TiO<sub>2</sub> film. The electrolyte solution was composed of 50 mM iodine (I<sub>2</sub>), 500 mM lithium iodide (LiI), and 500 mM *tert*-butyl pyridine dissolved in acetonitrile. Platinized ITO/glasses were used as counter electrodes to fabricate the DSSCs.

### 2.2. Characterization

The microstructure and morphologies of the graded films were observed by using a scanning electron microscope (SEM, LEO 1530, Germany), a transmission electron microscope (TEM, JEOL JEM-200CX, 200 kV, Japan), and a high-resolution transmission electron microscope (HRTEM, JEOL JEM-2010, Japan). The pore size distribution in the films was determined using a nitrogen adsorption–desorption apparatus (ASAP 2010, Micromeritics Instrument Corporation, Germany) through the BJH (Barrett–Joyner–Halenda) method.

Photovoltaic properties of the fabricated DSSCs were measured under light irradiation with a solar simulator (91192, Oriol, USA) at an intensity of 100 mW/cm<sup>2</sup> with a black mask. The active area of the DSSCs was 0.235 cm<sup>2</sup>.

## 3. Results and discussion

### 3.1. Design of the graded structure films

Particles of different sizes should match well with each other in a good graded film. In this section, we will design an optimal graded structure with binary particles, P25 particles, and the small particles. It is supposed that P25 particles will form the frame of the graded film and the small particles will fill up the voids formed by P25 particles' pileup. The possible range of the content of the small particles in the graded structure can be calculated as follows.

Here, we set the volume of the film as unity, and the porosity of P25 particles and the small particles as  $\varepsilon_1$  and  $\varepsilon_2$ , respectively. According to our assumption that the small particles would exist in the voids between P25 particles, the overall porosity of the graded film is  $\varepsilon_1\varepsilon_2$ . When the volume fraction of P25 particles in the two particles is set as  $\phi_1$  and that of the small particles is  $\phi_2$  ( $\phi_1 + \phi_2 = 1$ ), the equations below will be obtained:

$$\phi_1 = \frac{1 - \varepsilon_1}{1 - \varepsilon_1\varepsilon_2} \quad (1)$$

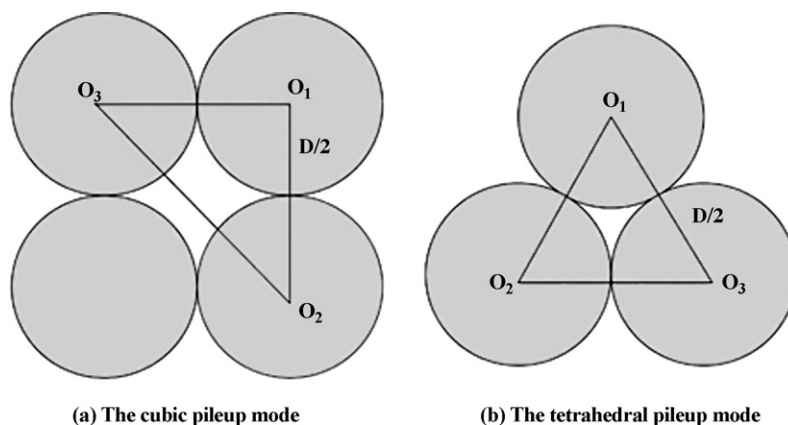


Fig. 1. The geometry diagram of the two limited pileup modes.  $O_i$  ( $i=1-3$ ) is the center of the relative particle.  $D$  is the diameter of particles.

$$\phi_2 = \frac{(1 - \varepsilon_2)\varepsilon_1}{1 - \varepsilon_1\varepsilon_2} \quad (2)$$

In practice, the small particles and P25 particles are mixed in the same manner, so the pileup modes of the two style particles are supposed to be similar. To simplify the calculation, it is assumed that  $\varepsilon_1 = \varepsilon_2 = \varepsilon$  here, therefore the equations below can be derived from Eqs. (1) and (2):

$$\phi_1 = \frac{1 - \varepsilon}{1 - \varepsilon^2} = \frac{1}{1 + \varepsilon} \quad (3)$$

$$\phi_2 = \frac{(1 - \varepsilon)\varepsilon}{1 - \varepsilon^2} = \frac{\varepsilon}{1 + \varepsilon} \quad (4)$$

Next, we will identify the range of  $\varepsilon$ . There are two special modes of certain particles' pileup, cubic mode and tetrahedral pileup mode, which represent the highest and the lowest  $\varepsilon$  of the particles' pileup, respectively, as shown in Fig. 1.

The porosity can be calculated as 0.4764 for the cubic mode and 0.2595 for the tetrahedral mode [18]. When all the particles are in the cubic mode,  $\varepsilon$  would be 0.4764 and  $\phi_2$  would be 32% according to Eq. (4). When all the particles are in the tetrahedral mode,  $\varepsilon$  would be 0.2595 and  $\phi_2$  would be 20.5% according to Eq. (4). However, there are particle interferences between graded particles, so the pileup of the two style particles is neither the pure cubic mode nor the pure tetrahedral mode. Thus, we can conclude that the optimum  $\varepsilon$  should be in the range between 0.2595 and 0.4764. What is more, the optimum volume fraction of the small particles should be in the range between 20.5% and 32%. Since the density of these two kinds of  $\text{TiO}_2$  particles can be regarded as the same, the optimum weight content of the small particles is also in the range between 20.5% and 32%.

### 3.2. Determination of the optimum ratio of the graded film

The content of the small particles in the graded film determines the photovoltaic performance of DSSCs. They not only fill up the voids between larger particles, but also bind the two particles together. It has been confirmed in Section 3.1 that the range of the optimum weight content of the small particles is 20.5–32%. Here, five kinds of paste 1 were designed with the small particle contents of 20.5%, 24.5%, 28.5%, 32.5%, and

35% relative to the sum of the two particles. When the content is beyond 35%, the graded paste is not viscous enough for deposition. The graded films were obtained by depositing the pastes on ITO/glass substrates, followed by heat treatment at 150 °C. DSSCs were assembled with the graded films as photoanodes. Fig. 2 shows the dependence of light-to-energy conversion efficiency of the cells on the weight content of the small particles. From Fig. 2, it is found that the efficiency first increases with the small particles' weight content then decreases when the content is beyond 28.5%. It is considered that the proper content of the small particles contributes to the good dispersion of the small particles between P25 particles, affords connections between P25 particles with chemical bonds, and increases the surface area of the graded film which, in turn, increases the adsorption of dyes. Therefore, the efficiency of the cells increases when the content of the small particles increases up to 28.5%. However, when the weight content is larger than 28.5%, excessive small particles would lead to the deterioration of the optimal graded structure and would increase interfaces in the graded film. The increased interface means more energy barriers that will affect the transport of photo-induced electrons in the graded structure. What is more, excessive small particles would affect the pore size distribution in the graded film and form smaller pores,

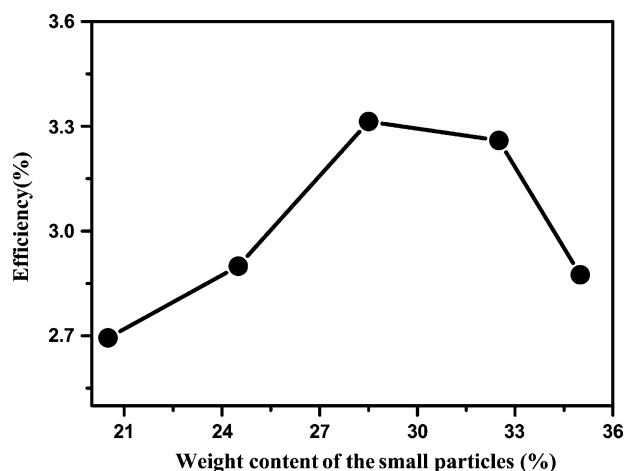


Fig. 2. Dependence of efficiency on the small particles weight content.

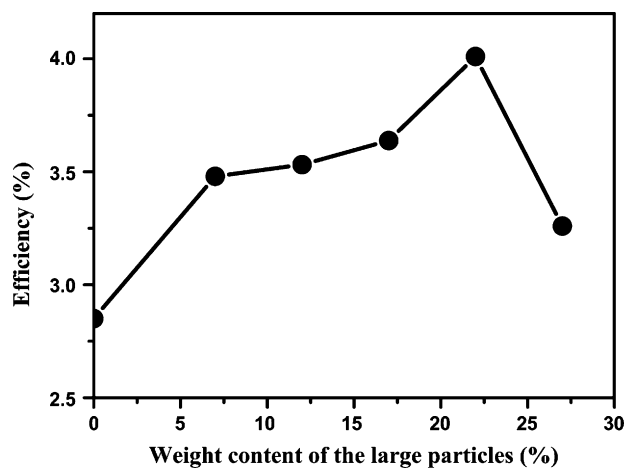


Fig. 3. Dependence of efficiency on the weight content of the large particles.

which would slow down the diffusion of electrolyte. Therefore, the efficiency decreases with the increase of the small particle content, and the 28.5% weight content of the small particles could be regarded as the optimum content for our films.

Larger particles (more than 100 nm) have been employed as light-scattering centers to increase the optical length in TiO<sub>2</sub> film, and several examples of enhanced light harvesting have been demonstrated both experimentally [19,20] and theoretically [21–23]. Here, the effects of the weight content of scattering particles in the graded structure films were also studied. Six kinds of paste 3 with the large particles (100 nm) having weight contents of 0%, 7%, 12%, 17%, 22%, and 27% relative to the total TiO<sub>2</sub> weight were designed here. The weight ratio of P25 particles versus the small particles was fixed at 5:2 according to the results above (the optimum weight content of the small particles was 28.5%). ITO/glass substrates and heat treatment temperature of 150 °C were applied. Fig. 3 shows the dependence of light-to-energy conversion efficiency of the cells on the weight content of the large particles. From Fig. 3, it is found that the efficiency first increases with the large particle weight content, indicating that the large particles did act as light-scattering centers. When the content of large particles is larger than 22%, the efficiency of the cell will drop down rapidly. This may be attributed to the lesser surface area in the graded films caused by excessive large particles. Thus, the best content of the large particles in the film should be 22%. According to the results above, the optimum weight ratio of P25 particles, the small particles, and the large particles in the graded film should be 5:2:2.

Because the large particles have a very small surface area (9 m<sup>2</sup>/g) and occupy 22 wt.% in all the three particles, the whole surface area would be reduced by adding the large particles. However, the small particles with a large surface area could compensate for such a reduction and even make it larger than pure P25 particles, which would be good for the photovoltaic performance of the cells. Fig. 4 shows the pore size distribution in the optimum graded structure film. The measuring sample was obtained by scraping powders from the substrate. The pores in the film vary between 5 and 75 nm, with a mean size at 35 nm. The BET results also show that the specific surface area reached

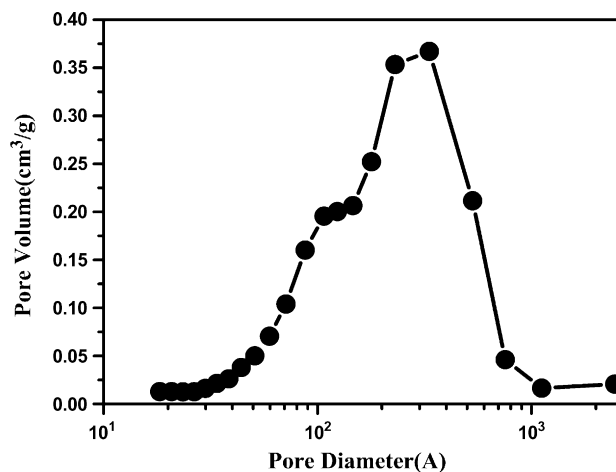


Fig. 4. Cumulative pore size distribution in the optimum graded structure film.

57.76 m<sup>2</sup>/g, a little larger than the surface area of P25 particles, which is 55 m<sup>2</sup>/g. What is more, the overall porosity was 29%, which was just in the range between 0.2595 and 0.4764 as referred above. This also verifies the validity of the results in Section 3.1.

### 3.3. Photovoltaic properties of the DSSCs with the graded films at low temperature

The final objective of the present study is to prepare photoanode films on conductive polymer substrates (e.g., ITO/PEN) at a low temperature and to assemble flexible DSSCs. However, heat treatment at a low temperature usually leads to weak connections and the subsequent high internal resistance of the films, which in turn lowers the current density and the efficiency of DSSCs. The effect of heat treatment on the graded films from room temperature to 450 °C was investigated in the present study. Paste 3 was deposited on ITO/glass substrates, followed by heat treatment at 20, 50, 80, 120, 150, and 450 °C. The weight ratio of the three sizes particles, namely, P25 particles, large particles, and small particles, in the paste was 5:2:2 according to the results above. Fig. 5 shows the dependence of the efficiency and the current

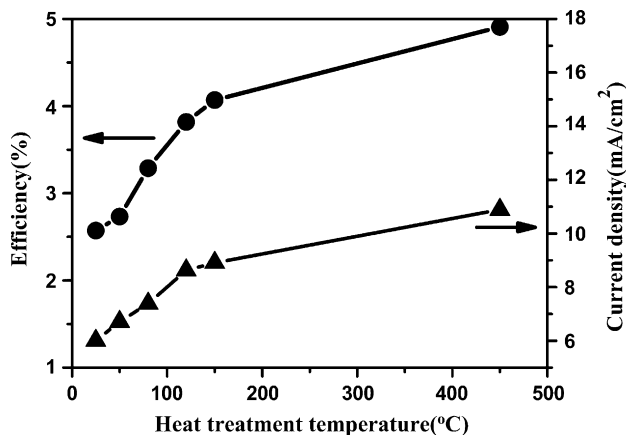


Fig. 5. Dependence of the efficiency and the current density on the heat-treatment temperature. The line with solid circle symbols represents the efficiency and the line with triangle symbols represents the current density.



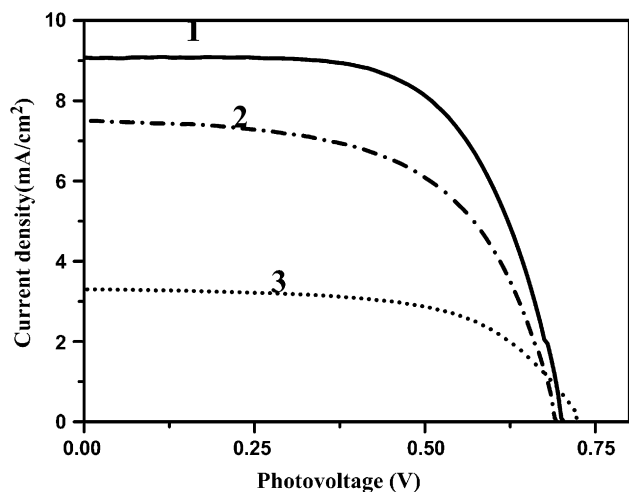


Fig. 6.  $I$ - $V$  curves of the typical DSSCs with the photoanode films treated at  $150^{\circ}\text{C}$ : (1) DSSC with the optimum graded structure film on an ITO/glass substrate; (2) DSSC with the optimum graded structure film on an ITO/PEN substrate; (3) DSSC with the pure P25 film on an ITO/PEN substrate.

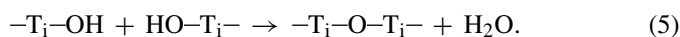
density on the heat treatment temperature. It has been found that the current density and the efficiency increase with temperature, which is in accordance with Miyasaka's work [16]. The efficiency for the cell with  $150^{\circ}\text{C}$  treated photoanode film is up to 4.1%, which is just a little lower than that of the DSSCs with a  $450^{\circ}\text{C}$  treated film. Even when it is treated at room temperature, the cell still shows an efficiency of 2.6%.

To assemble a flexible DSSC, the optimum graded structure film has been deposited on an ITO/PEN substrate treated at  $150^{\circ}\text{C}$ . For comparison, a pure P25 film with a thickness of  $4\ \mu\text{m}$  was also deposited on the ITO/PEN substrate. Fig. 6 shows the photovoltaic properties of a DSSC with the optimum graded structure film on an ITO/glass substrate, a DSSC with the optimum graded structure film on an ITO/PEN substrate, and a DSSC with the pure P25 film on an ITO/PEN substrate. Under standard testing conditions, the cell based on the ITO/glass substrate gave a photocurrent density of  $I_{\text{sc}} = 9.1 \pm 0.2\ \text{mA}/\text{cm}^2$ , an

open circuit voltage of  $V_{\text{oc}} = 0.705\ \text{V}$ , and a fill factor of  $\text{ff} = 0.64$ , yielding a 4.10% conversion efficiency as shown in curve (1). Meanwhile the cell based on the ITO/PEN substrate gave a photocurrent density of  $I_{\text{sc}} = 7.5 \pm 0.2\ \text{mA}/\text{cm}^2$ , an open circuit potential of  $V_{\text{oc}} = 0.69\ \text{V}$ , and a fill factor of  $\text{ff} = 0.59$ , yielding a 3.05% conversion efficiency as shown in curve (2). The efficiency of the former is just 25.6% higher than that of the latter. For the cell of the pure P25 film on the ITO/PEN substrate, it gave a photocurrent density of  $I_{\text{sc}} = 3.3 \pm 0.1\ \text{mA}/\text{cm}^2$ , an open circuit potential of  $V_{\text{oc}} = 0.720\ \text{V}$ , and a fill factor of  $\text{ff} = 0.61$ , yielding only 1.45% conversion efficiency as shown in curve (3).

### 3.4. Discussion for the structure of the graded film

The good performance of the designed graded films at a low temperature may be attributed to the chemical sintering process [14] during the low-temperature treatment. The small particles were synthesized by hydrothermal method in an acid environment. The pH value of the resulting sols, referred to as precursor 1 before, was ca. 1 [17], and there were many  $-\text{OH}$  groups in the surfaces of the small particles. Once P25 particles were mixed with the precursor,  $-\text{OH}$  groups would be adsorbed by the surfaces of P25 particles. When such a graded structure was heated at a low temperature,  $-\text{OH}$  groups on the small particles and P25 particles would lead to the reaction of dehydration, as shown in Eq. (5) [16]:



The dehydration would increase the physical and chemical connections not only between the small particles and P25 particles, but also between the small particles in the graded film, and then reduce the internal resistance of the film.

This definitely improves the photovoltaic performance of the DSSCs even with low temperature-treated photoanode films. At the same time, with the binding effect of the small particles and the appropriate pileup by the optimum ratio, the mechanical strength should be improved.

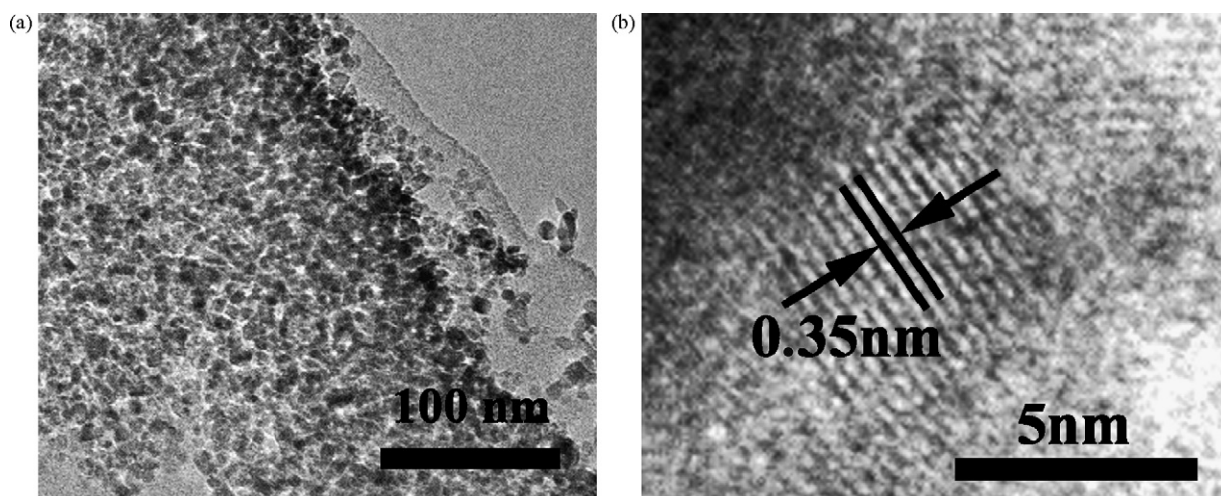


Fig. 7. Characterizations of the small particles in precursor 1: (a) TEM image and (b) HRTEM image. The spacing between adjacent layers in (b) is 0.35 nm, corresponding to the distance between (101) planes in an anatase phase structure.

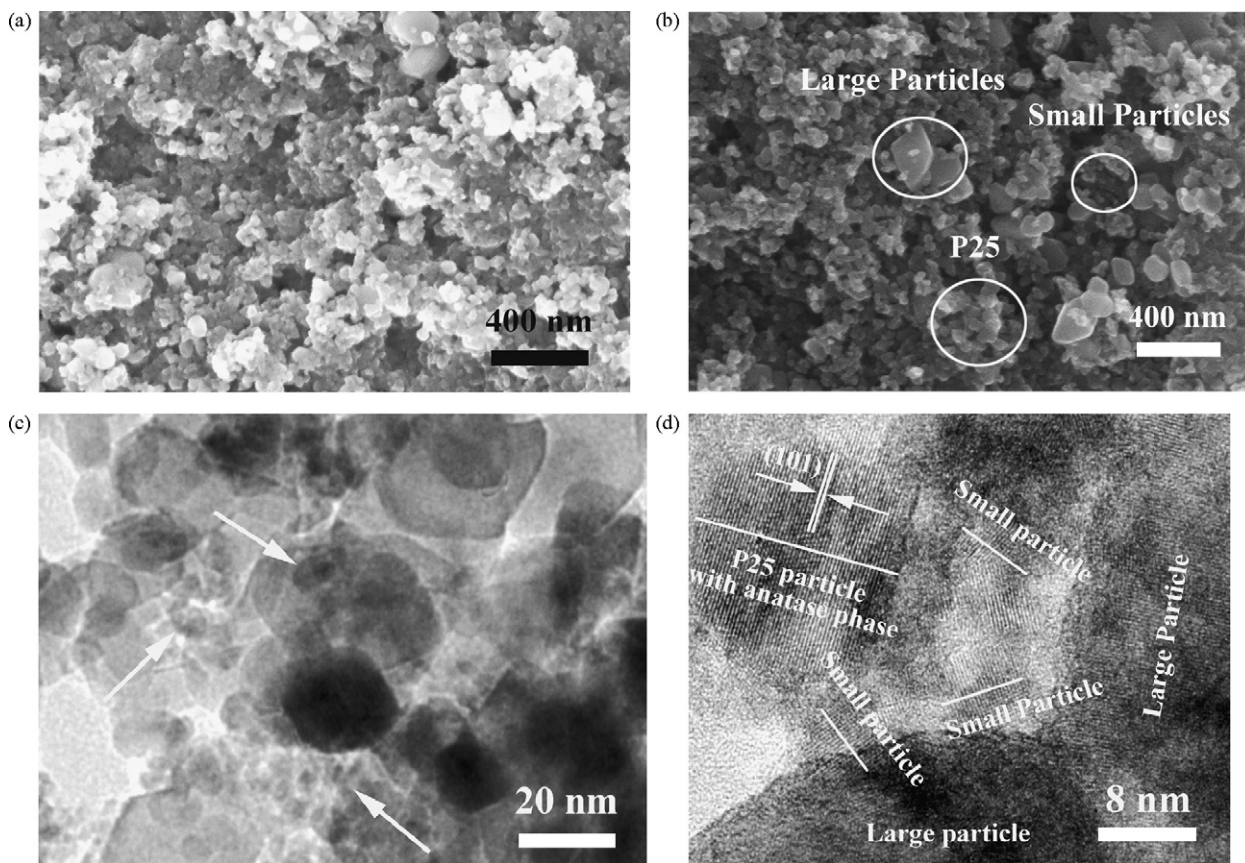


Fig. 8. SEM images of (a) surface and (b) cross-section of the graded film; (c) TEM image and (d) HRTEM image of the graded film. The arrows in (c) indicate the small particles filling in the pores of larger particles. Several small particles connecting P25 particle and two large particles are shown in (d).

To realize the chemical sintering process above and the function of the small particles in the graded film, no aggregation of the small particles in sols and their good dispersion into larger particles are required. The hydrothermal synthesis of the small particles in an acid environment assures such requirements. Fig. 7a shows the TEM image of the small particles in sols. From Fig. 7a, it is found that the small particles' size ranges from 7 to 12 nm and is well dispersed in the precursor, which contributes to the accommodations of the small particles between larger particles as shown in Fig. 8. An HRTEM (Fig. 7b) image shows that the small particles are crystalline, and the anatase phase, which is preferably used in DSSCs, is confirmed again by the faces oriented along the (101) direction.

Fig. 8 shows the microstructure of a typical graded film with a heat treatment temperature of 150 °C. The weight ratio of the three kinds of particles, P25 particles, the large particles, and the small particles, is 5:2:2. From Fig. 8a (surface SEM image) and b (cross-section SEM image), it can be found that the graded film has a uniform, mesoporous, and crack-free structure. The different kinds of particles are dispersed homogeneously in the films. The mesoporous structure, which provides a large surface area for adsorbing the dyes, was produced by the proper ratio of different particles, although no polymer was added in the paste to make pores. The crack-free structure means that the small particles act well as a binder to connect larger particles at a relatively low temperature of 150 °C. In fact, the typical

graded film showed good mechanical strength and cannot be easily erased by hand.

The TEM image shows the pileup microstructure of the typical graded film. The TEM samples and the SEM samples are from the same graded film. Some small particles fill in the pores in the pileup of P25 particles as shown in Fig. 8c. Several small particles are found to connect a P25 particle and two large particles in Fig. 8d. The small particles in the voids between the larger particles lead to the good connections between the larger particles, which contribute to the formation of a mechanically stable film and to the good transport of the photo-induced electrons in the graded film.

#### 4. Conclusions

Graded films that underwent low-temperature treatment have been designed as photoanodes of flexible DSSCs. The graded film has a uniform, mesoporous, and crack-free structure. The effect of the relative ratio of binary graded particles (P25 particles and the small particles) on the photovoltaic performance of DSSCs was investigated. Large particles were added to the binary graded film as scattering particles. The optimum weight content of the three kinds of particles was determined as P25 particles:the small particles:the large particles=5:2:2. The small particles act well as a binder to connect other larger particles and contributed to the large sur-

face area for adsorbing the dyes. Encouraging efficiency of the cell on the ITO/glass substrate with low-temperature treatment at 150 °C was achieved as 4.1%, which is just 19.5% lower than that of the DSSCs heat-treated at 450 °C. Furthermore, efficiency of the cell on the ITO/PEN substrate is up to 3.05%. With further optimization of the particles' size, film thickness, and electrolyte composition with dyes, a better photovoltaic performance of flexible DSSCs would be obtained.

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