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# Comparison of low crystallinity $TiO_2$ film with nanocrystalline anatase film for dye-sensitized solar cells

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ABSTRACT

Dye adsorption and microstructure of $TiO_2$ film are important properties when it is used as photoelectrode of dye-sensitized solar cells (DSCs). This study investigated the application of a low crystallinity $TiO_2$ film in DSCs. The low crystallinity $TiO_2$ film is composed of interconnected spherical particles with an average size of 20 nm and has homogeneous mesoporous inner structure. A DSC based on the anatase nanocrystalline mesoporous film prepared by P25 was used for comparison purpose. It is shown that although loaded with much less dye, the DSC based on the low crystallinity $TiO_2$ film generated $I_{sc}$ (short circuit photocurrent) as much as the one based on the conventional anatase nanocrystalline film does and obtained higher $V_{oc}$ (open circuit photovoltage) as well as *ff* (fill factor). The overall light-to-electricity efficiency ($\eta$) of the DSC based on the low crystallinity $TiO_2$ film reached 5.37%, while the $\eta$ of the DSC based on anatase nanocrystalline film was 4.69% in this work condition. It is suggested that a low crystallinity $TiO_2$ mesoporous film with a proper microstructure is as efficient as the anatase nanocrystalline mesoporous film when used in DSCs.



## 1. Introduction

Dye-sensitized solar cells (DSCs) have attracted great attention over the past decades since they were developed by Grätzel in 1980s [1] because of their low-cost, environment friendliness and high efficiency photovoltaics compared to silicon cells [2]. A mesoporous network of interconnected nanometer-sized $TiO_2$ crystallines has been used as the photoelectrode in DSCs, which serves as both electron acceptor and transport layer adsorbed with a monolayer of a sensitizer dye for light absorption. The dye is excited by light and injects an electron into the conduction band of $TiO_2$ and then regenerated by the electron donation from the electrolyte, usually an organic solvent containing a redox system, such as the iodide/triiodide couple. The iodide is regenerated in turn by the reduction of triiodide at the counter-electrode. The circuit is completed via electron migration through the external load.

The anatase phase of $TiO_2$ nanocrystalline mesoporous film is the most important photoelectrode material in DSCs. The $TiO_2$ nanocrystalline mesoporous film is composed of anatase nanoparticles with an average size of 20 nm, which provides a high surface area to adsorb a large amount of dye. Besides, the facets of the bipyramidal shape of the anatase nanoparticles have (101) orientation corresponding to the anatase crystal planes with the lowest surface energy, so high capability to adsorb dye [3]. Therefore high crystallinity of anatase has been required for $TiO_2$ mesoporous film applied to the photoelectrode of DSCs. On the other hand, low crystallinity or amorphousness $TiO_2$ has poor (101) facets to adsorb dye inefficiently and shapeless low crystallinity or amorphousness $TiO_2$ particles cannot provide a homogeneous mesoporous inner structure for the film, which are the primary disadvantages to performance of DSCs. Therefore, a low crystallinity or amorphousness $TiO_2$ film is usually avoided to be used in DSCs. S. Hao et al. found that the $TiO_2$ films prepared by sol–gel method consisted of a lot of irregular amorphousness or low crystallinity phase and had poor photoelectric performance with a $\eta$ of 0.8%. However, the $TiO_2$ films prepared by both P25 nanometer powder and hydrothermal method consisted of highly crystallized phases and exhibited much better performance. Therefore they believed that it was important for $TiO_2$ film to behave highly crystallized nanoparticles anatase [4]. T.N. Murakami et al. treated the anatase nanocrystalline film with chemical vapor deposition (CVD) of Ti alkoxide and found that amorphous $TiO_2$ layer derived from CVD process at 80–100 °C had a lower level of dye adsorption than non-treated anatase nanocrystalline film, which resulted in a loss in optical absorption and obtained a $\eta$ of 2.7% [5]. Kun Hou et al. concluded

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that a low light to electricity conversion efficiency of $TiO_2$ film may related extremely to the low crystallinity of the titania matrix film according to their experimental results [6]. Therefore, it seems important to use highly crystallized titania film as the photo-electrode of DSCs.

As mentioned previously, high efficient DSC requires high crystallinity of anatase. However, it is very difficult to produce well crystallized $TiO_2$ with such a small size of about 20 nm. $TiO_2$ films with different crystallinity degree exhibited fluctuated efficiencies of DSCs under the same conditions [7]. The performances of a low crystallinity or amorphousness $TiO_2$ dose not fluctuate with the crystallinity degree of $TiO_2$. This means that low crystallinity $TiO_2$ film is expected to have stable performance when used as a photo-electrode of DSCs. In addition, the preparation of a low crystallinity $TiO_2$ is simpler than anatase nanocrystalline because it does not need to control crystal growth. In this study, a novel low crystallinity $TiO_2$ film with homogeneous mesoporous inner structure of interconnected spherical particles with an average size of 20 nm was prepared by the Tetrahydrofuran modified reverse microemulsion method as described in the previous paper [8], and was used in DSC. Its performances, such as short circuit photocurrent ($I_{sc}$), open circuit photovoltage ($V_{oc}$), fill factor ($ff$) and the overall light-to-electricity efficiency ($\eta$), were investigated and compared with those of the anatase nanocrystalline mesoporous film prepared by P25.

## 2. Materials and methods

### 2.1. Materials

All chemicals used are analytical grade. Cetyltrimethylammonium bromide (CTAB), *n*-butyl alcohol, *cis*-di(thiocyanato)-*N*,*N*′-bis(2,2′-bipyridyl-4-carboxylate-4′-tetrabutyl ammonium carboxylate)ruthenium(II) (N719), cyclohexane, Tetrahydrofuran (THF), Tetrabutyl titanate, diethanolamine, LiI, $I_2$, *tert*-buthylpyridine (TBP), acetonitrile (ACN), acetylacetone (ACA), P25 (Degussa), distilled water and Triton X-100 were used as received. Conducting glass plates (FTO, sheet resistance is 25 $\Omega/cm^{-2}$) were used as the substrate for depositing $TiO_2$ film.

### 2.2. Preparation of $TiO_2$ mesoporous electrodes

The preparation of low crystallinity titania mesoporous film was as follows: first, tetrabutyl titanate and diethanolamine were mixed together with a molar ratio of 1:1 as starting reactants. Diethanolamine acted as a hydrolytic inhibiter. CTAB, *n*-butyl alcohol, cyclohexane and water were mixed with a mass ratio of 1:1:8:2 to get transparent reverse microemulsion. Next, THF, with a mass ratio of 1:3 to CTAB, was added into the microemulsion. The quinary reverse microemulsion was stirred for a few minutes, then the mixture of tetrabutyl titanate and diethanolamine was added into the microemulsion and stirred for several minutes at 60 °C to get an opalescent colloid precursor. Using Scotch tape as spacers, the resulting $TiO_2$ colloid solution was coated onto conducting glass plates and dried at 120 °C for ten minutes to remove the water and organic components, then annealed at 450 °C for half an hour in an oven to remove the surfactant CTAB and then formed a homogeneous $TiO_2$ mesoporous thin film. A thicker film is produced by repeating the coating, drying and annealing steps. The area of the film was 1 $cm^2$. The resulting low crystallinity $TiO_2$ mesoporous film was denoted as AM–$TiO_2$.

For comparison purpose, a nanocrystalline $TiO_2$ mesoporous film made of P25 nano-powder, a commercial $TiO_2$ containing mainly anatase, was prepared by the following steps: P25 was treated by diluted nitric acid (pH 1) for 24 h at 80 °C, then dried. The resulting powder was mixed with acetylacetone (ACA), distilled water and Triton X-100 at a mass ratio of 2:1:5:0.5 and then grinded for 4 h to get highly dispersed P25 slurry. The P25 slurry was coated onto the conducting glass plates and dried for five minutes at 120 °C, and then annealed at 450 °C for half an hour in an oven to form the nanocrystalline $TiO_2$ mesoporous film. A thicker film is produced by repeating the coating, drying and annealing steps. The area of the film was 1 $cm^2$. The resulting nanocrystalline $TiO_2$ mesoporous film was denoted as CM–$TiO_2$.

### 2.3. DSC fabrication

After sintering process, the mesoporous $TiO_2$ electrodes were cooled to about 80 °C and then immersed in an ethanol solution of N719 over night for dye-adsorption. The dye-adsorbed $TiO_2$ electrodes were clamped with the counter electrode (a platinised FTO) into a sandwich-type cell. A drop of electrolyte solution (0.1 M LiI, 0.05 M $I_2$ and 0.5 M TBP in ACN) was injected into the space between the clamped electrodes.

### 2.4. Measurements and characterization

The shape, size and dispersion of $TiO_2$ nano-particles as well as the morphology of the mesoporous $TiO_2$ film were characterized by a Leo-Supra35 field-emission scanning electron microscopy (FE-SEM). The shape, size and dispersion of $TiO_2$ nano-particles in the colloid precursor were characterized by a Philpsa-TecnAI 10 transmission electron microscopy (TEM). The crystal structures of the samples were characterized by a Philips PW 1830 X-ray diffractmeter (XRD) using Ni-filtered Cu$K_\alpha$ radiation ($\lambda = 1.54056$ Å). The thickness of $TiO_2$ film was measured by a Stylus Profiler.

The photocurrent-voltage characteristics were measured with a potentiostat (chi660a) under illumination. A 1000 W Xenon lamp was employed as the light source in conjunction with an IRA-25S filter (Schott, USA) to get rid of the UV light. The light intensity corresponding to AM 1.5 (100 $mW/cm^2$) was calibrated using a standard silicon solar cell. The photovoltaic characteristics of DSC were obtained by applying an external potential bias to the cell and measuring the generated photocurrent. The voltage step and delay time of the photocurrent were 10 mV and 40 ms, respectively. It was confirmed that the I–V curve showed no hysteresis under these conditions.

The amount of adsorbed dye was determined by desorbing the dye from the titania surface into NaOH aqueous solution (pH 13) and measuring its absorption spectrum. The concentration of adsorbed dye was analyzed by a UV–vis spectrophotometer (SP-2102UV).

## 3. Results and discussion

### 3.1. Microstructure of AM–$TiO_2$ and CM–$TiO_2$

Fig. 1a shows the microstructure of AM–$TiO_2$ and the inset shows the synthesized $TiO_2$ nanoparticles in the colloid precursor. The synthesized $TiO_2$ are globular and highly dispersed nanoparticles with a narrow size-distribution of about 20 nm. The AM–$TiO_2$ is a homogeneous thin film with mesoporous inner-structure formed by interconnected $TiO_2$ nano-particles, just like the CM–$TiO_2$ shown in Fig. 1b.

Fig. 2 shows the XRD spectra of AM–$TiO_2$ and CM–$TiO_2$ respectively. The samples are films with the area of 1 $cm^2$ and the thickness of 15 μm. The XRD spectrum of CM–$TiO_2$ shows distinguishable peaks at $2\theta$ of 25.47° and 47.98°, the characteristic peaks for anatase. However the XRD spectrum of AM–$TiO_2$ shows weak and diffusing peaks at 25.47° and 47.98°, which means that the $TiO_2$ film is poorly crystallized and mostly amorphous.