Reduction Electron Recombination of Dye-sensitized Solar Cells based on TiO₂ Spheres Consisting of Untrathin Nanosheets with [001] facet exposed

Hongxia Wang, * Meinan Liu, Cheng Yan, John Bell

School of Engineering Systems, Queensland University of Technology, 2 George Street, GPO Box 2434, Brisbane, QLD 4001, Australia

Abstract:
An anatase TiO₂ material with hierarchical structured spheres consisting of untrathin nanosheets with 100% [001] facet exposed was employed to fabricate dye-sensitized solar cells (DSCs). Investigation of the electron transport and back reaction of the DSCs by electrochemical impedance spectroscopy showed that the spheres had a 3-fold lower electron recombination rate compared to the conventional TiO₂ nanoparticles. In contrast, the effective electron diffusion coefficient, Dₑ, was not sensitive to the variation of the TiO₂ morphology. The TiO₂ spheres showed the same Dₑ with that of the nanoparticles. The influence of TiCl₄ post-treatment on the conduction band of the TiO₂ spheres and on the kinetics of electron transport and back reactions was also investigated. It was found that the TiCl₄ post-treatment caused a downward shift of the TiO₂ conduction band edge by 30 meV. Meanwhile, a 4-fold increase of the effective electron lifetime of the DSC was also observed after TiCl₄ treatment. The synergetic effect of the variation of the TiO₂ conduction band and the electron recombination determined the open circuit voltage of the DSC.

Keywords: TiO₂ [001] facet, dye-sensitized solar cells, electron recombination, electrochemical impedance spectroscopy, untrathin nanosheet

Introduction
In the past two decades, dye-sensitized solar cells (DSCs) have received substantial attention from both academic and industrial communities as one of the most promising low cost, high efficiency third generation photovoltaic devices [1,2]. A typical DSC consists of a dye coated TiO₂ electrode
which is deposited on a fluorine doped tin oxide (FTO) conductive glass substrate, a I/I₃⁻ redox couple based electrolyte and a platinum counter electrode. Upon illumination, the photo with high energy (higher than the energy difference between the HOMO and LUMO level of the dye molecule) excite an electron from the ground state of the dye molecule to its excited state. The electron is then injected to the conduction band of the adjacent TiO₂ material owing to a favorable energetics alignment. The electron goes through a series of trapping/detrapping process in the TiO₂ film before reaching the current collector based on the fluorine doped tin oxide (FTO) conductive substrate. Meanwhile, a parallel reaction which involves transferring the hole from the oxidized state of the dye (dye⁺) to the surrounding I⁻ ions of the redox couple of the electrolyte occurs to regenerate the dye molecule, resulting in the formation of I₃⁻ ions. The electrical circuit is completed through transferring the electron which arrives at the Pt counter electrode through external circuit to the I₃⁻ ions of the electrolyte.

Apparently, the operation of a DSC depends on several reactions which occur at the interface between different materials [3]. In particular, the process of electron injection at the interface of TiO₂/dye and the electron recombination reaction at the interface of TiO₂/dye/electrolyte are critical because they control both the short circuit current and open circuit voltage of the DSC. The surface property of the TiO₂ material plays an important role in both processes. The electron injection process in DSCs is controlled by the energy difference between the conduction band of TiO₂ material and the LUMO level of the dye, and the electron recombination process is mainly dominated by the interaction between the electron at the surface of TiO₂ and I₃⁻ ions in the electrolyte. Generally, the TiO₂ used in DSCs is based on anatase phase with [101] facet exposed due to the robust stability of this surface compared to other crystal facet [4]. It has been reported that the average surface energy of different facet of anatase TiO₂ has the order of [001] (0.90 J/m²) > [100] (0.53 J/m²) > [101] (0.44 J/m²) [5]. Apparently, the lowest surface energy of [101] facet is the most stable surface in TiO₂ material. With the progress of synthesis technique, other active facets of TiO₂ crystals such as [001] which is normally unstable due to a higher surface energy can now be made however [6]. In practice, TiO₂ material with a large percentage of [001] high energy surface has shown superior performance in
applications such as water splitting and lithium ion battery [6-8]. Further investigation shows that the [001] surface is beneficial to the photooxidization process through the O\(^-\) centres compared to the [101] surface which contains more Ti\(^{3+}\) centres [9].

The different surface property of the [001] and [101] facet of TiO\(_2\) is expected to have profound effect on the chemicophysical processes in DSCs as well. Fan et al have reported that the [001] surface can absorb more dye molecules compared to the [101] surface [10]. However, the influence of TiO\(_2\) [001] facet on the kinetics of electron transfer and back reaction has not been reported. A deep understanding of the role of TiO\(_2\) [001] facet in these key processes of electron transport and recombination of DSCs is of great importance for both practical applications and basic research.

In this work, anatase TiO\(_2\) spheres with a hierarchical structure consisting of ultrathin nanosheets with 100% [001] facet exposed were synthesized and applied in dye-sensitized solar cells (DSCs). The photovoltaic performance of the DSCs with different concentration of the hierarchical structured TiO\(_2\) spheres was evaluated. The kinetics of electron transport and back reaction of the DSCs with the spheres were investigated by electrochemical impedance spectroscopy. In addition, the effect of TiCl\(_4\) aqueous solution treatment on the performance of the DSCs with the TiO\(_2\) spheres was discussed.

**Experimental**

*Synthesis of TiO\(_2\) nanosheet particles*

Hierarchical structured TiO\(_2\) spheres of the nanosheets were synthesized by following the method which was originally reported by Chen et al [6]. Briefly, a precursor solution containing titanium isopropoxide (Sigma-Aldrich) (1.15 ml) and diethylenetriamine (DETA) (0.02 ml) in 32 ml isopropanol was prepared by magnetic-stirring the mixture of the three components vigorously at room temperature. The precursor solution was then transferred to a Teflon-lined stainless steel autoclave (45 ml volume, Parr Instrument Co.) for the hydrothermal reaction. The hydrothermal process was carried out at 200 °C for 24 h in an electric oven. After that, the autoclave was cooled to room temperature naturally. The as-collected white powder was washed with deionized water and
then ethanol for several times to remove the organic residues. The powder was then dried at 80°C for 5 h and then sintered at 400 °C for 3 h to improve the crystallinity.

**Fabrication of TiO$_2$ paste**

TiO$_2$ pastes for the DSCs were fabricated by mixing methylcellulose (Mw = 20,000), α-terpinol and the as-prepared TiO$_2$ powder with controlled amount using magnetic stirring at 80 °C for 48 h. Two sets of paste with different concentration of the TiO$_2$ powder were prepared. Paste A contained 13 wt% TiO$_2$ powder, 2.6 wt% methylcellulose and 84.4 wt% α-terpinol. Paste B contained 25 wt% TiO$_2$ powder, 2.5 wt% methylcellulose and 72.5 wt% α-terpinol. A commercial TiO$_2$ paste (DSL-18-NR, Dyesol) consisting of anatase TiO$_2$ nanoparticles with an average size of 20 nm was employed for comparison.

**Assembly of dye-sensitized solar cells**

The procedure for fabrication of the dye-sensitized solar cells has been reported in our previous work [11,12]. Briefly, a substrate based on fluorine doped tin oxide (FTO) conductive glass (TEC15, Pilkington) was thoroughly washed with detergent water, distilled water, acetone, isopropanol and ethanol in sequence under sonication for 15 mins. The cleaned FTO substrate was first coated with a compact layer of TiO$_2$ film by spray pyrolysis to reduce the electron back reaction at the interface of bare FTO and the electrolyte. The substrate was then deposited with the as-prepared TiO$_2$ paste or the commercial paste by a doctor-blading method using a Schotch tape as a spacer to control the thickness of the film. The TiO$_2$ film was dried on a hotplate at 90 °C for 10 mins before being sintered at 450 °C for 30 mins to form a mesoporous structure. The average thickness of the TiO$_2$ film was 13 μm. TiO$_2$ film with TiCl$_4$ post-treatment was carried out by immersing the sintered film in TiCl$_4$ aqueous solution (40 mM) at 70 °C for 30 mins. The film was washed with distilled water thoroughly and blow dried with N$_2$ gas. The film was then resintered at 450 °C for 30 mins. The geometrical area of the TiO$_2$ film was 0.25 cm$^2$.

The TiO$_2$ film (with or without TiCl$_4$ treatment) when it was still warm (around 80 °C) was immersed in a dye solution containing 0.25 mM cis-bis(isothiocyanato) bis(2,2′-bipyridyl-4,4’-dicarboxylate) ruthenium(II) bis-tetrabutylammonium (N719, Dyesol) in ethanol for 16 hours to form a dye coated
photoanode. A platinum counter electrode was prepared by dropping 5 μl isopropanol solution containing H3PtCl6·6H2O (5 mM) on a cleaned FTO substrate (1.5 ×1.0 cm²). After dry in air, the substrate was then sintered at 390 °C for 15 mins in an electric oven to form a thin Pt layer on the FTO substrate. A dye-sensitized solar cell was assembled by sealing the dye coated TiO2 electrode with the platinized FTO counter electrode using a thermal plastics (Surlyn 1705) at 130 °C. The electrolyte composed of 0.6 M 1-propyl-3-methylimidazolium iodide, 0.05 M I2, 0.1 M guanidinium thiocyanate, 0.2 M NaI, 0.1 M N-methyl benzimidazole in 3-methoxypropionitrile was introduced into the space between the electrodes through the holes which were predrilled in the Pt counter electrode by a vacuum-assisted technique. The holes were then sealed using a Surlyn film covered with a microscope slip.

**Characterization**

The morphology and the crystal structure of the as-prepared TiO2 powder were investigated by scanning electron microscope (SEM, FEI Quanta 200) and powder X-ray diffraction (XRD, PANanalytical Xpert Pro), respectively. Transmission electron microscopy (TEM, Philips CM 200) was used to monitor the detailed structure of the TiO2 powder. The thickness of the TiO2 films for the DSCs was determined by a profilometer (Dektak 150). The photocurrent density-voltage (J-V) characteristics of the DSCs was obtained using a Xe lamp (150 W) based solar simulator (Newport) by recording the current of the cells as a function of the applied bias under AM1.5 illumination (100 mW/cm²) with a computer-controlled digital source meter (Keithley 2420). The illumination intensity of the incident light from the solar simulator was measured with a silicon photodiode which was calibrated with an optical meter (1918-C, Oriel). Aluminum foil with size comparable to the active area of the TiO2 film was used as reflector on the counter electrode side of the DSCs during the J-V measurement.

The electrochemical impedance spectroscopy (EIS) of the DSCs was measured in the frequency range of 50,000 - 0.1 Hz at room temperature by a Versa-stat 3 electrochemical workstation (Princeton Applied Research). The EIS measurement was carried out under illumination which was provided by
a light emitting diode (LED, 627 nm) at open-circuit. The intensity of the incident illumination on the front side of the DSC (TiO$_2$ side) was adjusted using a combination of neutral density filters. The EIS spectrum was analysed with a Zview software using a transmission line based equivalent circuit to obtain the information of chemical capacitance, electron recombination resistance and electron transport resistance of the DSCs [12,13].

3. Results and discussions

Figure 1(a) shows the image of the as-prepared TiO$_2$ powder by SEM. The material consists of micro-sized particles with sphere shape. The surface of the sphere is very rough and seems fluffy. The diameter of the sphere is around 1.6 µm as determined by TEM (Figure 1b). TEM images (Figure 1b and c) also illustrate that the sphere has sub-structure which is consisting of unthathin nanosheets that are packed together. It is speculated that the sphere is formed through self-assembly of the nanosheets to realize a minimum surface energy. Some spheres have pits on the surface which may be due to the insufficient reaction duration. The measurement of the N$_2$ adsorption/ desorption isotherms of the TiO$_2$ powder shows that the specific surface area of the TiO$_2$ spheres is 82 m$^2$/g, which is slightly higher than the specific surface area of the film made from the commercial TiO$_2$ paste (DSL-18NR, Dyesol. Surface area: 72.9 m$^2$/g) [14]. The large surface area of the material suggests that the nanosheets are probably loosely packed so that more surface areas are exposed. The XRD pattern of the material (Figure 1(d)) shows that the as-prepared TiO$_2$ powder is anatase with a tetragonal structure and space group $I4_1/amd$ (JCPDS card, No. 71-1169). Both the TEM images and the XRD results are in good agreement with the results reported by Chen et al. According to Chen et al, the TiO$_2$ spheres synthesized by this method have 100% [001] surface exposed [6].

The SEM image of the TiO$_2$ film consisting of the spheres is shown in Figure 1(e) and Figure 1(f). Apparently, the TiO$_2$ particles are connected with each other in the film. Figure 1(f) shows that the film contains large amount of small pores. However, the sphere of the TiO$_2$ particles is rarely seen in the film. This indicates that the mechanical force of grinding and sonication employed in the preparation of the film broke up the spheres into small particles, probably in the form of nanosheets.
Nevertheless, the same XRD pattern of the sintered TiO$_2$ film (not shown) indicates that the film has the same surface property with the spheres.

Figure 1. Images of TiO$_2$ particles by SEM (a) and by TEM (b, c) as well as XRD pattern of the TiO$_2$ particles (d) and morphology of the TiO$_2$ film consisting of the as-prepared sphere particles (e, f).
J-V characteristics of the DSCs

The J-V characteristics of the DSCs with the TiO₂ film made from paste A which contained 13 wt% TiO₂ spheres with and without TiCl₄ post-treatment is shown in Figure 2(a). The DSC solely based on paste A without TiCl₄ treatment (Curve A) produced a short circuit current density ($J_{sc}$) of 8.79 mA/cm² and open circuit voltage ($V_{oc}$) of 0.76 V. In contrast, when the TiO₂ film was subject to TiCl₄ solution treatment, the $J_{sc}$ of the DSC (curve B) is increased to 12.1 mA/cm², which is 37.5% higher than that of Curve A.

Figure 2(b) shows the J-V performance of the DSCs made from Paste B which contains 25 wt% as-prepared TiO₂ nanosheet based particles. The $J_{sc}$ of the cell is 15.6 mA/cm² and $V_{oc}$ = 0.70 V (Figure 2(b), Curve C) when there was no TiCl₄ treatment. Compared to Curve A, it is found that the ratio of the $J_{sc}$ of Curve C to that of Curve A ($(15.6 \text{ mA/cm}^2)/(12.1 \text{ mA/cm}^2) = 1.77$) is very close to the ratio of the concentration of the TiO₂ spheres in the two pastes ($(\text{TiO}_2 \text{ wt% in paste B})/(\text{TiO}_2 \text{ wt% in paste A}) = (25)/(13) = 1.92$). It suggests that the higher $J_{sc}$ of the DSC made from Paste B is due to the availability of more TiO₂ particles in the film which can absorb more dye molecules, leading to a higher light absorption. The $J_{sc}$ of the DSC made from Paste B is further increased from 15.6 mA/cm² (Figure 2(b), Curve C) to 18.2 mA/cm² when the TiO₂ film was processed with TiCl₄ solution (Figure 2(b), Curve D). Meanwhile, the $V_{oc}$ of Curve D is 20 mV higher than that of Curve C, suggesting the beneficial effect of TiCl₄ post-treatment on $V_{oc}$ as well. The best performance is obtained with curve D with power conversion efficiency = 7.57% (Figure 2(b)), which is comparable to the efficiency ($\eta=7.52\%$) of the DSCs (I-V curve is not shown) made from the commercial paste. The detailed characteristic parameters of the performance of the DSCs with different TiO₂ pastes are shown in Table 1.
Figure 2: $J$-$V$ characteristics of the dye-sensitized solar cells made from Paste A containing 13 wt% TiO$_2$ spheres (a) and from Paste B containing 25 wt% spheres (b) with (Curve B and D) and without (Curve A and C) TiCl$_4$ treatment

Table 1. Characteristic performance parameters of the dye-sensitized solar cells

| Cell name                                           | $J_{sc}$ (mA/cm$^2$) | $V_{oc}$ (V) | $FF$ | Efficiency (%) |
|-----------------------------------------------------|-----------------------|--------------|------|----------------|
| 13 wt% TiO$_2$ nanosheet (Curve A)                  | 8.79                  | 0.757        | 0.7  | 4.66           |
| 13 wt% TiO$_2$ nanosheet with TiCl$_4$ treatment    | 12.07                 | 0.754        | 0.646| 5.88           |
| (Curve B)                                           |                       |              |      |                |
| 25 wt% TiO$_2$ nanosheet (Curve C)                  | 15.6                  | 0.7          | 0.61 | 6.66           |
| 25 wt% TiO$_2$ nanosheet with TiCl$_4$ treatment    | 18.2                  | 0.72         | 0.58 | 7.57           |
| (Curve D)                                           |                       |              |      |                |
| DSC made from TiO$_2$ nanoparticles                 | 16.5                  | 0.755        | 0.604| 7.52           |

**Electrochemical Impedance spectroscopy**

The information on the charge transfer and transport process in DSCs can be measured by small perturbation based transient methods such as electrochemical impedance spectroscopy (EIS) or intensity modulated photocurrent spectroscopy (IMPS) and intensity modulated photovoltage spectroscopy (IMVS) [13,15]. Compared to IMPS and IMVS, the advantage of EIS method for
characterization of DSCs lies in that both the effective electron lifetime, $\tau_n$, and the effective electron diffusion coefficient, $D_n$, can be obtained in one measurement. This is achieved by fitting the EIS spectrum using a suitable equivalent circuit that mimicks the physical process in the device. The equivalent circuit which depicts the process of electron trapping/detrapping in DSCs is shown in Figure 3(a). It contains a series resistance, $R_s$, a capacitance at Pt electrode/electrolyte interface, $C_{Pt}$, and a resistance for the charge transfer process between electrons at Pt electrode and $I_3^-$ ions of the electrolyte, $R_{Pt}$. $Z_w$ is the Warburg resistance arising from the ion transport in the electrolyte and $Z_d$ is a distribution line describing the electron transport and recombination in the mesoporous TiO$_2$ film [13,16]. A typical EIS spectrum of a DSC is shown in Figure 3(b) for the Nyquist plot and Figure 3(c) for the Bode plot. The corresponding fitting results (green line) using the equivalent circuit are also shown in Figure 3 (b, c). The distorted semicircle in the high frequency range (above 10 Hz) is ascribed to the electron transfer process at the interface of Pt counter electrode/electrolyte combined with the electron transport process in the TiO$_2$ film (the semicircle corresponding to the electron transport process in TiO$_2$ is buried in the semicircle of the charge transfer process at Pt/electrolyte interface in the spectrum) [3]. The large semicircle in the lower frequency range (10 - 0.1 Hz) is due to the electron recombination process in the TiO$_2$ film. Under a high incident illumination intensity, the density of the photo-generated electron in the TiO$_2$ film is very high (up to $10^{18}$/cm$^3$) and the TiO$_2$ film becomes conductive [17]. In this case, the resistance corresponding to the electron transport process becomes too small to be observed in the EIS spectrum. Consequently, the EIS spectrum is mainly dominated by the electron recombination process. Nevertheless, under a low incident illumination intensity, the conductivity of the TiO$_2$ film is very low due to a low density of the photo-generated electron. In this case, the main feature of the EIS spectrum is due to the transport of electron in the TiO$_2$ film. Hence, an accurate fitting of the EIS spectrum of a DSC using the equivalent circuit is normally obtained in the illumination range when both the electron transport resistance and the electron recombination resistance are substantial [13]. Only the results from good fittings are shown in this work.
Figure 3. Equivalent circuit (a) and the Nyquist plot (b) and Bode plot (c) of the impedance spectrum of a dye-sensitized solar cell

Comparison of electron transport and recombination of the DSC based on TiO\textsubscript{2} spheres and nanoparticles

The electron recombination process in DSCs is reflected by the effective electron lifetime, $\tau_n$ whereas the electron transport process is manifested by the effective electron diffusion coefficient $D_n$. Bisquert et al have shown that both $\tau_n$ and $D_n$ of a DSC are dependent on the distribution of density of electron in the conduction band (free electron) and in the trap states (trapped electron) of the TiO\textsubscript{2} film as well as the lifetime and diffusion coefficient of free electron ($\tau_0$ and $D_0$) through the following consideration

\[
\tau_n = \left(1 + \frac{\partial n_t}{\partial n_c}\right)\tau_0 \quad \text{(Eq.1)}
\]

and

\[
D_n = \left(1 + \frac{\partial n_t}{\partial n_c}\right)^{-1}D_0 \quad \text{(Eq.2)}
\]
where \( n_t \) and \( n_c \) are the density of the trapped electron and free electron respectively [18].

The charge distribution, \( g(E) \), in a mesoporous TiO\(_2\) film is described by [18,19]:

\[
g_n(E_F) = \frac{N_{t,0}}{k_BT_0} \exp\left(\frac{E_n - E_F}{k_BT_0}\right) = \frac{N_{t,0}}{k_BT_0} \exp\left(\frac{E_n - E_{F,\text{redox}} - qV}{k_BT_0}\right)
\]  
(Eq.3)

Where \( \mu E_F \) is the quasi-Fermi level of TiO\(_2\), \( E_n \) the conduction band of TiO\(_2\), and \( E_{F,\text{redox}} \) the potential energy of the redox couple, \( N_{t,0} \) the total density of the trapped electron, \( k_B \) is the Boltzmann constant and \( T_0 \) the characteristic temperature which reflects the profile of the charge distribution in TiO\(_2\).

Therefore, comparison of the change of \( \tau_n \) and \( D_n \) in DSCs due to the different material component should be made by using density of charge as the reference provided that the distribution profile of charge density is the same [20].

Because the density of charge in the TiO\(_2\) film is reflected by the chemical capacitance, \( C_\mu \), which is measured by EIS, through the relationship [18]:

\[
C_\mu(E,F) = \int_{E_n}^{E} C_\mu(E,F,E) dE \approx q^2 \int g_n(E_F) dE
\]  
(Eq.4)

We employ density of chemical capacitance as the reference for the investigation of the variation of \( \tau_n \) and \( D_n \) in the following.

Figure 4(a) shows the \( \tau_n \) of the DSCs with the TiO\(_2\) films consisting of the nanosheets based spheres and the conventional nanoparticles as a function of the chemical capacitance density. It is found that \( \tau_n \) of the nanosheets based DSC is nearly 3-fold higher than that of the nanoparticles for a constant capacitance density. It suggests that the TiO\(_2\) film with the spheres has a lower electron recombination reaction rate compared to the film with the nanoparticles. Besides \( \tau_n \), the effective electron diffusion coefficient, \( D_n \), is another important parameter which controls the performance of a DSC. The comparison of the \( D_n \) of the cell based on the spheres and the nanoparticles is shown in Figure 4(b). It is interesting that both materials show the same \( D_n \), suggesting that the electron transport is not affected by the morphology and the exposed crystal facet of TiO\(_2\) material. The identical \( D_n \) also suggests that the diffusion coefficient of the free electron is the same for the two materials according to Eq.2 [13]. It also justifies the assumption that the profile of the distribution of charge density is the same in the two types of TiO\(_2\) film. In constrast, the different \( \tau_n \) suggests that the free electron
lifetime of the spheres is different from that of the nanoparticles. The low \( \tau_n \) of the spheres could be related with the property of the [001] facet, but clarification of this issue needs more investigations. As a consequence, the electron diffusion length, \( L_n \), which depends on both the \( \tau_n \) and \( D_n \) by \( L_n = \sqrt{\tau_n D_n} \), is up to 1.6-fold higher for the nanosheet based TiO\(_2\) spheres than that of the nanoparticles (Figure 4(c)). It is found that the \( L_n \) of the DSC based on the nanoparticles is only around 16 \( \mu \)m (Figure 4(c)), which is comparable to the thickness of the TiO\(_2\) film (13 \( \mu \)m). Previous study has shown that the \( L_n \) of a DSC needs to be at least 3-fold the thickness of the TiO\(_2\) film in order to collect most of the photogenerated electrons [13]. Therefore, the short \( L_n \) may limit the performance of the DSC. The higher \( L_n \) of the spheres based DSC should benefit a higher electron collection efficiency compared to the nanoparticles counterpart.

Besides \( J_{sc} \), \( V_{oc} \) is another key performance parameter of a DSC. The maximum voltage of a DSC is determined by the potential difference between the conduction band of TiO\(_2\) and the redox potential of I\(/I^-\) in the electrolyte. Obviously, the position of the TiO\(_2\) conduction band edge, \( E_c \), has direct impact on the open circuit voltage (\( V_{oc} \)) of the DSC. Thus it is important to know the relative position of the \( E_c \) of the nanosheets based spheres relative to the nanoparticles in order to disclose the reason for the different \( V_{oc} \). According to Equation 3, the change of \( E_c \) of TiO\(_2\) can be monitored by the variation of the voltage (\( V \)) of the DSC at a constant electron density.

As shown in Figure 4(d), the \( E_c \) of the nanosheet based spheres is found to be 100 meV lower than that of the nanoparticles. The lower \( E_c \) of the spheres is probably due to the different dye uploading on the TiO\(_2\) films. According to Fan et al [10], TiO\(_2\) [001] facet can absorb more dyes than the [101] facet. Nazeeruddin et al have confirmed that the dye molecule is adsorbed on TiO\(_2\) particles mainly through the carboxy acid group (–COOH) [4], leading to the protonation of the surface of TiO\(_2\) and the downward shift of the \( E_c \). The more dye molecules are adsorbed on the TiO\(_2\) film, the more downward shift is expected for the \( E_c \).
Figure 4. Comparison of the effective electron lifetime, $\tau_{\text{ne}}$, (a) and effective electron diffusion coefficient, $D_n$, (b) and electron diffusion length, $L_n$, (c) of the DSCs with TiO$_2$ nanosheets (open circle) and with conventional nanoparticles (solid circle). (d) Variation of the chemical capacitance density of the nanosheets and nanoparticles as a function of voltage.

Effect of TiCl$_4$ treatment

The strategy of treating TiO$_2$ mesoporous film with TiCl$_4$ aqueous solution has extensively been employed to improve the performance of DSCs. In most cases, it is found that the $J_{sc}$ of the DSC is enhanced while the $V_{oc}$ is reduced after the TiCl$_4$ treatment of the film. O’Regan et al found that TiCl$_4$ treatment caused 80 meV downward shift of the TiO$_2$ conduction band, resulting in an increased driving force for the electron injection process. They reported that the enhanced $J_{sc}$ was owing to an improved electron injection efficiency of the DSC [21,22]. In the following section, the influence of
the TiCl₄ solution treatment on the $E_c$ of the TiO₂ spheres based film and on the kinetics of electron transport and back reaction of the corresponding DSCs is investigated.

Figure 5 (a) illustrates the chemical capacitance density as a function of the voltage of the DSCs made from paste B with and without TiCl₄ treatment. It is found that, at a constant charge density, the voltage of the cell with TiCl₄ treatment is lower than that of the DSC without the treatment. The maximum difference in voltage between the cells is around 30 mV. Provided that the distribution profile of the charge density is the same of the TiO₂ film with and without TiCl₄ treatment, the reduced potential of the DSC with TiCl₄ treatment means that the TiCl₄ treatment caused a downward-shift of the TiO₂ conduction band by 30 meV, which may decrease the maximum voltage the DSC can achieve. This observation is in good agreement with the results reported by O’Regan et al [21]. However, the $V_{oc}$ of the cell with TiCl₄ treatment is actually 20 mV higher than the DSC without the treatment as shown in Figure 2(b). This indicates that the electron recombination of the DSC is probably affected by the TiCl₄ treatment.

Figure 5(b) shows the $\tau_n$ as a function of capacitance density of the DSC with and without TiCl₄ treatment. It is found that $\tau_n$ is enhanced by 3.8-fold after TiCl₄ treatment. In contrast, $D_n$ of the DSCs is relatively unchanged with the TiCl₄ treatment (Figure 5(c)). Owing to the enhanced $\tau_n$, the electron diffusion length, $L_n$, of the DSC is enhanced by two-fold through TiCl₄ treatment (Figure 5(d)). Hence, the improved voltage (20 mV) of the DSC (Figure 2(b), curve D) with TiCl₄ treatment compared to the cell without TiCl₄ treatment (curve C in Figure 2(b)) should be a result of the synergistic effect of the decreased TiO₂ conduction band and the increased electron lifetime. Apparently, the beneficial effect of the enhanced electron lifetime on $V_{oc}$ surpasses the negative effect of the downward-shift of the $E_c$ of TiO₂, leading to a higher $V_{oc}$. 


Figure 5. Comparison of dye-sensitized solar cells based on hierarchical structured TiO$_2$ spheres with and without TiCl$_4$ post-treatment. (a): chemical capacitance vs Voltage; (b): effective electron lifetime, $\tau_n$, as a function of charge density; (c): effective electron diffusion coefficient, $D_n$, as a function of charge density; and (d): electron diffusion length, $L_n$ as a function of voltage.

**Conclusion**

Dye-sensitized solar cells with TiO$_2$ electrode made from hierarchical structured TiO$_2$ spheres consisting of nanosheets with 100% [001] facet exposed were assembled and characterized in terms of the device performance, the kinetics of electron transport and back reaction. It was found that the TiO$_2$ spheres based DSCs generated an energy conversion efficiency of 7.57%, which is comparable to the conventional TiO$_2$ nanoparticles. Investigation of the kinetics of electron transport and back reaction of the DSCs showed that the spheres had a 3-fold higher effective electron lifetime compared to the
nanoparticles. However, the effective electron diffusion coefficient, $D_n$, of the DSCs was not affected by the different morphology and crystal facets exposed of the TiO$_2$ material. Monitor the variation of the conduction band of the dyed TiO$_2$ film disclosed that the $E_c$ of the spheres based TiO$_2$ electrode was 100 meV lower than that of the nanoparticles.

This work also investigated the influence of TiCl$_4$ aqueous solution treatment on the $E_c$ of the TiO$_2$ spheres and on the $\tau_n$ and $D_n$ of the corresponding DSCs. It was found that TiCl$_4$ treatment caused a downward shift (30 meV) of the TiO$_2$ conduction band and four-fold increase of the $\tau_n$ whereas the $D_n$ of the cell was not significantly affected by TiCl$_4$ treatment.

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