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Preparation of Hollow Titanium Dioxide Shell Thin Films from Aqueous Solution of Ti-Lactate Complex for Dye-Sensitized Solar Cells

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1. Introduction

As photovoltaic devices possessing potential for low processing costs and flexible architectures, dye-sensitized solar cells (DSSCs) using nanocrystalline TiO$_2$ (nc-TiO$_2$) electrodes have been extensively studied. (Bisquert et al., 2004; O’Regan & Grätzel, 1991) Congruently with increasingly urgent dissemination of solar cells against crisis of a depletion of fossil fuel, DSSCs are as promising alternative to conventional silicon-type solar cells. The main trend of investigations of DSSCs originates from the epoch-making works by Grätzel and co-workers in the early 1990s. (O’Regan & Grätzel, 1991) A typical construction of the cells are composed of dye-molecules (usually Ru complexes) coated nc-TiO$_2$ electrodes on transparent-conductive (TC) backcontact (usually fluorine-doped tin oxide (FTO)) glass substrate and counter Pt electrodes sandwiching triiodine/iodine [$I_3^−/I^−$] redox liquid electrolyte layer maintaining electrical connection with the counter Pt electrode. The voids of the network of TiO$_2$ nanoparticles connection form nanopores which are efficiently filled with electrolyte solution. An operation mechanism of DSSC begins with harvesting incident light by dye-molecules via photoexcitation of electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The photoexcited electrons are transferred to the conduction band of the nc-TiO$_2$ and diffuse in TiO$_2$ matrix to TC layer followed by ejection to outer electric load. The oxidized dye is reduced by the electrolyte ($I^−$) and the positive charge is transported to Pt counter electrode. As well as close fitting of photo-absorption spectra of dyes to the spectrum of sunlight mainly in visible light region (nearly panchromatic dyes) (Nazeeruddin et al., 2001) the strong dye-TiO$_2$ coupling leading to rapid electron transfer from excited dye to TiO$_2$ (Tachibana et al., 1996) realizes practically promising solar-to-electrical conversion efficiency: more than 10%. The charge separation of DSSCs occurs at the interface TiO$_2$ nanoparticles / dye molecules / [$I^−/I_3^−$] electrolyte. Therefore the combination of Ru-complex and TiO$_2$ is currently almost ideal choice in DSSC. Some problems of the TiO$_2$ nanoparticles electrode, however, remain room to investigate. Connection points of TiO$_2$ nanoparticles decrease an effective area of interface, and play a role on electron scattering sites, leading to restrict the conversion efficiency. (Enright & Fizmaurice, 1996; Peng et al., 2003) Though denser films seemingly improve the electron migration, they result in decrease of surface area for dye adsorption. Additionally TiO$_2$ nanoparticles electrodes are...
usually prepared by embrocation methods, e. g., a squeegee method, whereas via these methods great amount of Ti resource is consumed.

For the settlement several nanostructures of TiO$_2$ electrodes for DSSCs containing the array of nanorods, (Kang et al., 2008) nanotubes (Kang et al., 2009; Paulose et al., 2008) and assembly of spherical hollow (Kondo et al., 2006) or hemispherical (Yang et al., 2008) shells have been proposed owing to their ordered structures leading to ordered electron transport and large surface area for small amount of titanium as depicted in Fig. 1.

![Fig. 1. Models of TiO$_2$ nano-structure electrode for DSSCs, (a) standard nanocrystalline particles, (b) nano tube or nano pillar arrays and (c) hollow shells.](image-url)

Some works on ordered and multilayered hollow TiO$_2$ shells, which are inverse opal structure, have shown photonic crystalline effects leading to red shift in incident photon-to-current conversion efficiency (IPCE). (Nishimura et al., 2003; Yip et al., 2008) Recently energy conversion efficiencies of DSSCs using inverse TiO$_2$ opal, including 1.8 %, (Guldin et al., 2010) 3.47 % (Kwak et al., 2009) and 4.5 % (Qi et al., 2009) have been reported. In the previous work we prepared hollow TiO$_2$ shell monolayer films by the electrolysis of an aqueous (NH$_4$)$_2$TiF$_6$ solution on complicated polystyrene (PS) particles-preadsorbed substrate followed by calcination. (Chigane et al., 2009) Among few papers (Karuppuchamy et al., 2001; Yamaguchi et al., 2005) reporting the electrolytic preparation of TiO$_2$ for DSSC anode, the previous work first reported the DSSC conversion efficiency (0.63 %) using TiO$_2$ film prepared via electrolysis to our knowledge. From standpoint of methodology for a preparation of TiO$_2$ films electrolyses (electrodeposition) from aqueous solutions are a low cost and low resource consuming fabrication techniques since the deposition reaction occurs only nearby substrate. The (NH$_4$)$_2$TiF$_6$ solution is stable for long term, being able to undergo repeated electrolyses. However some industrial problems: liberation of highly toxic F$^-$ during electrochemical deposition reaction leading to bad working environment. Moreover insufficient conversion efficiency calls multilayered hollow structures. As a water-soluble and environment-benign titanium compound titanium bis(ammonium lactato)dihydroxide (TALH) increasingly attracts attention. (Caruso et al., 2001; Rouse & Ferguson, 2002) Especially Ruani and co-workers (Ruani et al., 2008) have developed single-step preparation of PS-TALH core-shell precursor from a suspension containing both PS and TALH, followed by fabrication inverse opal TiO$_2$ films by calcination. The process seems to be simple and time-saving compared with other conventional methods: PS template followed by infiltration of Ti oxides or Ti compounds sol. (Galusha et al., 2008; King et al., 2005; Liu et al., 2010; Nishimura et al., 2002) However DSSC electrode properties of the film have not been
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2. Experimental

Two types of PS possessing anionic (A-PS) and cationic (C-PS) functional group on the surface, prepared by an emulsifier-free emulsion polymerization of styrene monomer with potassium persulfate (KPS) and 2,2’-azobisisobutyronitrile (AIBN) as a radical initiator, respectively, were used. (Watanabe et al., 2007) From SEM observations a diameter of A-PS and C-PS beads was ca. 400 nm and ca. 300 nm, respectively. A TC glass plate coated with fluorine-doped tin oxide (FTO, 10 Ω/square, ASAHI GLASS Co., Ltd, A11DU80) and quartz glass plate (1 mm of thickness) were used as substrates. As pretreatments of substrates, FTO (15 mm × 20 mm) was degreased by anodic polarization (+5 mA cm⁻²) against Pt counter electrode for 30 s in a 1 mol dm⁻³ NaOH and quartz glass plate (20 mm × 40 mm) was immersed in a 10 % NaOH solution for 10 min at 333 K. Both substrates were thoroughly rinsed with deionized water and immersed in the colloidal suspension of PS and TALH in a cylindrical glass bottle being bent backward at about 60° against bottom. (Hartsuiker & Vos, 2008; Ye et al., 2001) The glass bottle containing the suspension and substrate was placed on a hot plate the temperature of surface of which was set at 345 K. In this way the temperature of the suspension was maintained at 325 K for 5–24 h until complete evaporation of water. The initial concentrations of PS and TALH in the suspension were 0.28 % and 0.0025 or 0.005 mol dm⁻³, respectively. Hollow shells TiO₂ (H-TiO₂) films were formed by the calcinations of the PS-TALH precursor at 723 K for 1 h. In the calcination, the temperature was raised in rate of 2 h...
from room temperature to 723 K. In some cases TiO\textsubscript{x} films were electrodeposited on the PS-TALH precursor films before calcination by a cathodic electrolysis in the electrolyte solution containing a 0.05 mol dm\textsuperscript{-3} TALH (Aldrich; reagent grade) and a 0.1 mol dm\textsuperscript{-3} NH\textsubscript{4}NO\textsubscript{3} at \(-2\) mA cm\textsuperscript{-2} of current density for 6 C cm\textsuperscript{-2} of charge density.

X-ray diffraction (XRD) patterns of the films in 3 cm\textsuperscript{2} of deposition area were recorded on a RIGAKU RINT 2500 diffractometer (Cu K\textsubscript{α}; \(\lambda = 0.1541\) nm; 40 kV; 100 mA), with the incident angle (\(\theta\)) fixed at 1°, scanning the diffraction angle (2\(\theta\)) stepwise by 0.05° with a counting time of 10 s.

Transmission spectra and relative diffuse reflection (DR) spectra in ultraviolet (UV)--visible range of hollow shells were measured by means of Shimadzu UV-3150 spectrometer. An integral spherical detector equipment (Shimadzu ISR-3100) was used for DR spectroscopy with BaSO\textsubscript{4} powder (Wako Pure Chemical Industries) as a reference reflector. For the powder sample the hollow shell film was detached from quartz glass substrate by scratching with spatula.

X-ray photoelectron (XP) spectra of the films were obtained by means of Kratos AXIS-ULTRA DLD. A monochromated Al K\textsubscript{α} (1486.6 eV; 150 W) line was used as the X-ray source. The pressure in the analyzing chamber was lower than \(<1\times10^{-8}\) Torr during measurements. Binding energies of Ti 2p and O 1s photoelectron peaks were corrected from the charge effect by referencing the C 1s signal of adventitious contamination hydrocarbon to be 284.8 eV.

For DSSC measurements, a composite TiO\textsubscript{2} (C-TiO\textsubscript{2}) film composed of flat bottom TiO\textsubscript{2} layer and hollow shell film was prepared. The deposition area, corresponding to an active area of the cell, was adjusted to be 0.25 cm\textsuperscript{2} using a mask. Initially TiO\textsubscript{x} film was galvanostatically electrodeposited on the FTO in the electrolyte solution containing a 0.05 mol dm\textsuperscript{-3} TALH (Aldrich; reagent grade) and a 0.1 mol dm\textsuperscript{-3} NH\textsubscript{4}NO\textsubscript{3} at \(-3\) mA cm\textsuperscript{-2} of current density for 10 C cm\textsuperscript{-2} of charge density as a blocking layer of DSSC electrode. On the FTO/TiO\textsubscript{x} layer the PS-TALH precursor was coated from aqueous suspension of 0.28 % C-PS and 0.0025 mol dm\textsuperscript{-3} TALH and thereon TiO\textsubscript{x} was coated by electrolysis. The TiO\textsubscript{2} hollow films on FTO substrates were immersed in an ethanolic solution of 0.3 mmol dm\textsuperscript{-3} ruthenium dye (bistetra butylammonium cis-di(thiocyanato)-bis(2,2'-bipyridine-4-carboxylic acid, 4'-carboxylate ruthenium(II), Solaronix N719) for 14–16 h at room temperature. An electrolyte solution for DSSC was composed of 0.1 mol dm\textsuperscript{-3} LiI, 0.05 mol dm\textsuperscript{-3} I\textsubscript{2}, 0.6 mol dm\textsuperscript{-3} 1,2-dimethyl-3-propylimidazolium iodine (DMPII, Solaronix) and 0.5 mol dm\textsuperscript{-3} 4-tert-butylpyridine in acetonitrile. A platinum-coated glass substrate was used for a counter electrode. The dye-coated TiO\textsubscript{2} electrode and the counter electrode were set sandwiching a separation polymer sheet (25\,\mu m of thickness; Solaronix SX-1170) and the electrolyte.

Photovoltaic current density (J)-voltage (V) curves were obtained using an instrument for the measurements of solar cell parameters (Bunkoh-Keiki Co., Ltd K0208, with a Keithley 2400) with photoirradiation by a 150 W xenon lamp under the condition that was simulated airmass 1.5 solar irradiance with the intensity of 100 mW cm\textsuperscript{-2}. Incident photon-to-electron conversion efficiency (IPCE) spectra ranging 400 to 800 nm of wavelength were measured by means of a spectral photosensitivity measurement system (Bunkoh-Keiki) with a 150 W xenon lamp light source. Calibration was performed using a standard silicon photodiode (Hamamatsu Photonics, S1337-1010BQ).

As a reference sample, TiO\textsubscript{2} nanocrystalline particles (nc-TiO\textsubscript{2}) electrode prepared by a squeegee method from TiO\textsubscript{2} colloidal solution (Solaronix Ti-Nanoxide D) and calcination in the same way as the hollow films was subjected to DSSC measurements.
The area density: amount of deposited TiO$_2$ against area (mg cm$^{-2}$) was determined using an X-ray fluorescent spectrometer (Rigaku RIX3100).

3. Results and discussion

3.1 Characterization of H-TiO$_2$ films

Figure 3 shows SEM photographs of PS-TALH precursors. For both A-PS and C-PS, the sizes of spherical PS-TALH units appeared to be almost same as PS itself and core/shell structures of PS/TALH were not clearly observed as shown in expanded images (Fig. 3(b) and (d)). Some bulgy junctions between adjacent spheres, however, suggest accumulation of TALH. From appearance with eyes and SEM images, PS particles and TALH were uniformly mixed.

![SEM photographs of PS-TALH films](image)

Fig. 3. Cross-sectional SEM photographs of PS-TALH films on FTO substrates from (a) or (b) A-PS and (c) or (d) C-PS, respectively.

Figure 4 shows SEM photographs of H-TiO$_2$ films. More than 20 layers of quasi-ordered spherical hollow shells were observed at some view points. The thickness of shell wall was ca. 10 nm. For the sample started from suspension containing A-PS and TALH 0.0025 mol dm$^{-3}$, the fcc configuration was observed especially on the surface in one to several millimeters range. However, the quasi-fcc ordered shells were discretely scattered on the substrate, and some parts of the substrate were not covered with films. On the other hand, although for the sample from C-PS the ordered structure was not observed (Fig. 4(d)) in micrometer view, the hollow shells smoothly coated almost all over the substrate. This more excellent dispersion by C-PS in appearance is due to uniform mixture of PS and
TALH in the precursor originating from their affinitive relationship. In both cases, there are observed many broken points of shells owing to PS-PS spheres contact at the initial precursor as shown in an inserted scheme in Fig. 4, leading to skeleton-like structure after calcinations.

![Cross-sectional or surface SEM photographs of H-TiO$_2$ films on FTO substrates prepared from (a) or (b) A-PS and (c) or (d) C-PS, respectively. Scale bars correspond 1 µm.](image-url)

Figure 4. Cross-sectional or surface SEM photographs of H-TiO$_2$ films on FTO substrates prepared from (a) or (b) A-PS and (c) or (d) C-PS, respectively. Scale bars correspond 1 µm.

Figure 5 shows XRD pattern of hollow shells film prepared on a quartz glass substrate by calcination of C-PS-TALH precursor. The pattern shows the TiO$_2$ shell film to be predominantly anatase type crystalline phase while the peaks were broad owing to nanocrystalline. (International Center for Diffraction Data, 1990)

The crystallite size ($D$) of the calcined film can be estimated from Scherrer’s formula (Kim et al., 2008)

$$D = \frac{0.89\lambda}{\beta\cos\theta}$$  \hspace{1cm} (1)

where $\lambda$ is the wavelength of the X-ray, $\beta$ is the peak width and $\theta$ is the Bragg angle of the peak.
Fig. 5. XRD patterns of (a) H-TiO₂ film on quartz glass substrate and (b) an authentic pattern of anatase-type TiO₂. (International Center for Diffraction Data, 1990)

Fig. 6. XP spectra of hollow TiO₂ film on quartz glass substrate prepared from C-PS (0.28 %) and 0.005 mol dm⁻³ TALH; (a) wide scan spectrum, (b) Ti 2p and (c) O 1s photoelectron spectra.
On the hypothesis that the sample is constituted by isotropic and spherical crystallites, the width of the most intensive X-ray diffraction peak, corresponding to anatase (101) plane at 25.273°, is adopted for the calculation of the \( \beta \) value. With the \( \beta \) value: 0.0153 (radian) obtained after the exclusion of the effect of \( K_a^2 \) line and optical system of the instrument, the D value is estimated to be 7.7 nm.

Figure 6 shows XP spectra of the surface of hollow shells film. In the wide energy range spectrum (Fig. 6 (a)) small peaks of Si 2p and Si 2s photoelectron originating from quartz glass substrate were observed as well as main titanium and oxygen peaks. Almost identical peak positions (within 1 eV) of Ti 2p\(_{3/2}\) region spectrum for the film and standard TiO\(_2\) (Chigane et al., 2009) at 458.9 and 458.7 eV, respectively, suggest that the chemical state of the hollow shells film can be assigned to TiO\(_2\). The main peak and secondary peak at 530 eV and at around 533 eV in O 1s photoelectron region spectrum can be attributed to titanium oxide (Ti-O-Ti) and silica of substrate, respectively, from references. (Moulder et al., 1992)

Figure 7 shows optical properties of H-TiO\(_2\) films prepared from C-PS and TALH.

Fig. 7. Relationship between H-TiO\(_2\) film on quartz glass substrate from C-PS-TALH and UV-visible photon energy: (a, solid line) transmission spectrum of the film and (b, dashed line) or (c, dotted line) diffuse reflection spectrum of film or powder sample, respectively and (d) Kubelka-Munk function plots for the powdered sample transformed from DR spectrum corresponding to (c).

Absence of clear attenuation dip in transmission spectrum indicates random configuration of hollow shells. Decrease and increase of transmittance and DR of film samples, respectively, according to photon energy up to ca. 3 eV are due to scattering of light by aggregation of TiO\(_2\) hollows. Taking account of DR of powder sample the decrease of both transmittance and DR of film sample at higher than 3 eV are due to interband photo-absorption of TiO\(_2\). Such change of DR of powder sample can be associated with absorption coefficient (\( \alpha \)) using Kubelka-Munk function (Kortümb, 1969; Murphy, 2007)

\[
F(R) = \frac{(1-R)^2}{2R} = \frac{\alpha}{S}
\]  

as shown in Fig. 7(d), where R and S indicate diffuse reflectance and scattering coefficient, respectively. Although all terms depend on energy (wavelength) of incident light, the sizes
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of hollow shells collectives (more than 1 \( \mu \text{m} \)) are enough larger than wavelength and in the wavelength range between 310 nm (ca. 4 eV) and 410 nm (ca. 3 eV) concerning photoabsorption (Fig. 7(c)) the change of \( S \) value might be little. Therefore in relation to absorption \( S \) can be assumed to be constant and then we investigated band edge using \( \alpha/S \) values. The relationship of \( \alpha \) and photon energy (hv) of semiconductors near the absorption edge region for direct or indirect transition is given by

\[
(\alpha h \nu)^2 = A(h \nu - E_g)
\]

or

\[
(\alpha h \nu)^{1/2} = A(h \nu - E_g)
\]

respectively, where \( A \) and \( E_g \) are proportion constant and band gap energy. (Pankove, 1971)

The linear relationship of Eq. (3) and (4) indicate that in the plots of \( (\alpha h \nu)^2 \) or \( (\alpha h \nu)^{1/2} \) versus hv the optical band gap can be determined by intersection of extrapolated straight line with \( h \nu \) axis. (Barton et al., 1999; Han et al., 2007; Nowak et al., 2009) Based on above mentioned assumption we derived the optical band gaps as 3.5 eV and 3.2 eV from intersection points of linear fitting line with \( (\alpha h \nu/S)^2 \) and \( (\alpha h \nu/S)^{1/2} \) versus \( h \nu \) for direct and indirect process, respectively, as shown in Fig. 8. At present we propose the latter value because 3.2 eV of \( E_g \) for anatase TiO\(_2\) is commonly accepted. (O’Regan & Grätzel, 1991; Tang et al., 1994) However more investigation is necessary since it has not been clarified whether interband transition of anatase TiO\(_2\) is direct or indirect. (Asahi et al., 2000; Mo & Ching, 1995)

Fig. 8. Plots of (a) \( (\alpha h \nu/S)^2 \) and (b) \( (\alpha h \nu/S)^{1/2} \) against UV-visible photon energy of powdered H-TiO\(_2\) transferred from \( a/S \) spectrum corresponding to Fig. 7(d). Linear lines are drawn to determine band gap energies.

3.2 Enhanced film quality by electrodeposition

Figure 9(a) shows low magnification SEM image of the films indicating considerable volume change by calcination. After calcination the film was constricted and broken apart as expected in introduction section. Moreover maybe owing to the stress by crystallization and plastic strain the film easily detached from substrate. Such poor quality of the films and
large crack made us expect low utility for DSSC electrode. Figure 9(b) and (c) show SEM images of TiO$_2$-coated H-TiO$_2$ film by electrodeposition before calcination. Although on the top surface view some narrow cracks were observed within 1 μm width, recognition of only hollow spheres in the back of the cracks indicates that the FTO substrate are not exposed. Cross-sectional view shows hollow shells suggesting successful maintenance of PS-TALH structure during electrodeposition.

![SEM photographs of H-TiO$_2$ films on FTO substrates](image)

Fig. 9. SEM photographs of H-TiO$_2$ films on FTO substrates; (a) or (b) surface view of the film without or with electrodeposition TiO$_x$ coating, respectively, and (c) cross-sectional view of the film with electrodeposition TiO$_x$ coating. In both cases the precursors are C-PS-TALH.

### 3.3 DSSC properties

Figure 10 and Table 1 show typical results of DSSC assessment for three type TiO$_2$ electrodes. The conversion efficiency value of the cell using only H-TiO$_2$ electrode: 0.91 % (Fig. 10(a)) was about 4 times lower than that for the cell: 3.98 % using standard nc-TiO$_2$ electrode (Fig. 10(b)). The conversion efficiency value of the cell using only H-TiO$_2$ electrode: 0.91 % (Fig. 10(a)) was about 4 times lower than that for the cell: 3.98 % using standard nc-TiO$_2$ electrode (Fig. 10(b)), despite 3.2 times smaller amount of TiO$_2$. There can be thought to be two reasons for such insufficient efficiency. One is lower short circuit current density ($J_{SC}$). The compli-cated morphology of hollow TiO$_2$ film might contribute to the increase of specific contact area.
with dye molecules and to harvesting light by scattering in the hollow shells. However a large number of broken points in the skeleton structure and few contact points with substrate supposedly leaded poor conduction of photo-induced electrons. The other is lower open circuit voltage ($V_{OC}$) due to direct contact between electrolyte solution and FTO substrate through wider film crack points. So as to improve the two problems we inserted initial flat TiO$_2$ layer on the substrate by electrolysis of TALH solution. Remarkably improved DSSC performance: 2.90 % for the composite (C-TiO$_2$) film composed of electrodeposited TiO$_2$ bottom layer and hollow TiO$_2$ top layer has been shown (Fig. 10(c) and Table 1) compared with single hollow layer (0.91 %), including enhancement of $V_{OC}$ and FF values. The area density of TiO$_2$ of nanoparticles electrode was as more than 2.4 times as the composite hollow shell film, whereas the change of the conversion efficiency was 1.4 times. This indicates the conversion efficiency per-TiO$_2$-weight for the composite hollow shell film is higher than nc-TiO$_2$ film owing to homogeneity effect of blocking layer making complicated structure of H-TiO$_2$ available.

![Figure 10](image.png)

Fig. 10. Photocurrent density voltage curves of DSSCs using (a) H-TiO$_2$, (b) nc-TiO$_2$ and (b) C-TiO$_2$ film. The cross-sectional SEM photograph indicates the C-TiO$_2$ sample corresponding to curve (c).

<table>
<thead>
<tr>
<th>TiO$_2$ films</th>
<th>Area density of TiO$_2$ / mg cm$^{-2}$ (by XRF)</th>
<th>$J_{SC}$ / mA cm$^{-2}$ $^a$</th>
<th>$V_{OC}$ / V $^b$</th>
<th>FF $^c$</th>
<th>Eff / % $^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hollow shell</td>
<td>0.179</td>
<td>2.19</td>
<td>0.716</td>
<td>0.580</td>
<td>0.911</td>
</tr>
<tr>
<td>Composite</td>
<td>0.244</td>
<td>5.85</td>
<td>0.805</td>
<td>0.615</td>
<td>2.90</td>
</tr>
<tr>
<td>Nano-particles</td>
<td>0.587</td>
<td>8.89</td>
<td>0.763</td>
<td>0.585</td>
<td>3.98</td>
</tr>
</tbody>
</table>

$^a$Short circuit current density. $^b$Open circuit voltage. $^c$Fill factor. $^d$Conversion efficiency.

Table 1. DSSC properties of two TiO$_2$ film electrodes.

Figure 11 shows IPCE assessments of cells using three type TiO$_2$ electrodes: nc-TiO$_2$, simply electrodeposited TiO$_2$ (E-TiO$_2$) and C-TiO$_2$ film. In this comparison we electrodeposited thicker first film than that in above J-V characterization. By this effect the conversion efficiency of C-TiO$_2$ film was somewhat enhanced to 3.44 %. The normalized IPCE curves for the films (Fig. 11(e), (f), (g)) have shown good spectral accordance of photocurrent with
photoabsorption of dye (Fig. 10(d)). Moreover heightening of composite TiO$_2$ film (Fig. 11(f)) by 14 % and 11 % at 450 nm and 600 nm of wavelength, respectively, against simple electrodeposited film (Fig. 11(e)), proves wavelength-independent increase of photocurrent by the addition of hollow shells as top layer. This seems to arise simply from increase of amount of TiO$_2$ and to imply low optical effect of our hollow shells, remaining what should be improved.

Fig. 11. IPCE spectra of DSSC using (a, dashed line) or (e, dashed line) E-TiO$_2$ film, (b, solid line) or (f, solid line) C-TiO$_2$ film and (c, dotted line) or (g, dotted line) nc-TiO$_2$ film.

4. Conclusions

Hollow TiO$_2$ (H-TiO$_2$) shell films have been prepared using environmentally benign Ti-lactate complex (TALH) as a titanium source. A precursor has been prepared from an aqueous colloidal suspension containing both polystyrene (PS) and TALH. Successive calcination of the PS-TALH precursor at 723 K led to the decomposition of PS and formation of hollow spherical shells. Employing PS with cationic surface functional group (C-PS) gave rise to smoothly spreading of hollow shells films in wider area compared with conventional PS possessing anionic groups (A-PS). The characterizations by X-ray diffraction and X-ray photoelectron spectroscopy have proved that the hollow shell films can be assigned to anatase TiO$_2$. Optical characteristics of H-TiO$_2$ films from C-PS-TALH have shown they are not in an inverse opal structure. Diffuse reflection spectroscopy combined with Kubelka-Munk treatment has revealed wide optical band gap as equal or more than 3.2 eV, indicating transparency of the films for visible light. It has been found that combination with electrodeposition of TiO$_x$ films strongly supports quality and DSSC properties of H-TiO$_2$ films in two aspects. First the electrodeposition onto the PS-TALH precursor film effectively prevented widely cracking in the calcination process. Moreover the electrodeposition onto FTO substrate before H-TiO$_2$ layer, namely fabrication of composite film (C-TiO$_2$ film), substantially enhanced DSSC energy conversion efficiency: 2.9 % which was comparable to an electrode using commercially available TiO$_2$ nanocrystalline particle (nc-TiO$_2$). The IPCE curve of C-TiO$_2$ film has revealed the increase of photocurrent due to light-harvesting effect.
On the other hand its independence of wavelength has indicated that H-TiO$_2$ lacks photonic crystal effect and then a future investigation on improvement of arraying of H-TiO$_2$ is needed.

5. References


Absorbance and Photocurrent in Dye-Sensitized Titanium Dioxide Photoelectrodes Coupled to Photonic Crystals, *Journal of the American Chemical Society*, Vol.125, No.20, pp 6306-6310, ISSN 0002-7863


The second book of the four-volume edition of "Solar cells" is devoted to dye-sensitized solar cells (DSSCs), which are considered to be extremely promising because they are made of low-cost materials with simple inexpensive manufacturing procedures and can be engineered into flexible sheets. DSSCs are emerged as a truly new class of energy conversion devices, which are representatives of the third generation solar technology. Mechanism of conversion of solar energy into electricity in these devices is quite peculiar. The achieved energy conversion efficiency in DSSCs is low, however, it has improved quickly in the last years. It is believed that DSSCs are still at the start of their development stage and will take a worthy place in the large-scale production for the future.

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