Improvement efficiency of a dye-sensitized solar cell using Eu\(^{3+}\) modified TiO\(_2\) nanoparticles as a secondary layer electrode†

Jing-Hong Huang,\(^a\) Po Yu Hung,\(^b\) Shu-Fen Hu*\(^b\) and Ru-Shi Liu*\(^a\)

Received 28th February 2010, Accepted 7th May 2010
DOI: 10.1039/c0jm00549e

This novel work presents the successful size control of Eu\(^{3+}\)-modified TiO\(_2\) nanoparticles by adding various amounts of Eu\(^{3+}\). The electronic structures of Eu\(^{3+}\)-modified TiO\(_2\) nanoparticles are different from those of pure TiO\(_2\) nanoparticles, as analyzed by DRS (UV-Vis diffuse reflectance spectroscopy) and XPS (X-ray photoelectron spectroscopy). As Eu\(^{3+}\)-modified TiO\(_2\) nanoparticles are used as a secondary layer in the double-layered electrode, the probability of recombination of excited electrons and holes is reduced to increase the short-circuit current (J\(_{SC}\)) during the operation of the dye-sensitized solar cells (DSSCs). The increase in the open circuit voltage (V\(_{oc}\)) from 0.66 to 0.71 V is observed owing to the energy of the conduction band in Eu\(^{3+}\)-modified TiO\(_2\) layer. Finally, the efficiency (\(\eta\)) is clearly improved from 2.20 to 3.43\% when the double-layered structure of Eu\(_{0.03}\)-TiO\(_2\)/Eu\(_{0}\)-TiO\(_2\) is adopted in the DSSCs.

1. Introduction

Dye-sensitized solar cells (DSSCs) have been identified recently as a third-generation technology, and extensively investigated by scientists in various fields. The advantages of dye-sensitized solar cells over similar earlier-generation technologies are the low cost of the materials, the lack of a need to use elaborate equipment to manufacture them and the possibility of engineering them as flexible sheets.\(^1,2\) The basic structure of DSSCs consists of five parts—the counter electrode, the electrolyte, the sensitizer, the conduction material/semiconductor and the FTO (fluorine-doped tin oxide) electrode. The working principle of a DSSC is that an electron in a dye molecule in the photoexcited state is injected through the conduction band of TiO\(_2\) into FTO, enabling the electron to be conducted into the outer circuit to drive the load and generate electric power. All circuits in a DSSCs must be made more efficient to promote the injection of electrons from dye molecules into the conduction material (FTO/TiO\(_2\)) and the suppression of the recombination of electrons and holes. Accordingly, TiO\(_2\) nanomaterials exhibit key electrical and physical properties that are exploited in their use as conduction materials in DSSCs, including good matching between the energy level of the conduction band and the photoexcited state of the dye molecule and the 3.2 eV band gap associated with the transmission of sunlight into a sensitizer. The difference between the potential of the conduction band of TiO\(_2\) and the photoexcited state of dye molecules drives the rapid injection of electrons into the conduction band of TiO\(_2\), but excited electrons are always lost in the interface between the dye molecules and the conduction layer, reducing the efficiency (\(\eta\)) of the DSSCs. The efficiency (\(\eta\)) of DSSCs has been improved using mixed oxides Ti\(_{1-x}\)Zr\(_x\)O\(_2\) conduction to change the band gap of the material.\(^3\)–6 When an electron is transferred from the photoexcited state of a molecular dye through the conduction band of TiO\(_2\) into FTO, the recombination of electrons and holes occurs frequently. The conduction material, such as TiO\(_2\), importantly determines the charge-transfer dynamics at the interface with the dye molecules, so it is important in the construction of desired TiO\(_2\) electrodes to improve the efficiency of DSSCs.

In this work, various sized Eu\(^{3+}\)-modified TiO\(_2\) nanoparticles are synthesized using the sol–gel and hydrothermal method by adding different amounts of Eu\(^{3+}\) with \(x\) from 0.003 to 0.04. Eu\(^{3+}\) ions can be used to modulate the structure of the conduction and valence bands of TiO\(_2\) nanoparticles to establish a double-layered TiO\(_2\) electrode. Herein, based on the double-layered structure of the Eu\(^{3+}\)-TiO\(_2\) electrode, the probability of recombination between electron and hole is reduced by arranging, as desired, the energy position of the conduction band to drive the forward injection of electrons into the FTO. When the double-layered electrode is used, the improvements in the DSSCs are evidenced by the open-circuit voltage (V\(_{oc}\)) and short-circuit current (I\(_{SC}\)). A black dye with wide-range absorption in wavelength is considered the most efficient absorption reagent for use in the sensitizer to convert light to electricity, when TiO\(_2\) is used as the conduction material in our study.\(^7,8\) The black dye absorbs from visible light to near infrared light with wavelengths of up to 900 nm, improving the overlap of absorbed wavelength by sensitizer with the solar spectrum.\(^9\)

2. Experimental section

2.1. Materials

[\(\text{Ti(OC}_4\text{H}_9)_4\)] (99%, Acroros), Eu\(_2\)O\(_3\) (99.9%, Sigma- Aldrich), nitric acid (37%, Sigma-Aldrich) and ethanol (99.98%, Sigma-Aldrich) were purchased without further purification. FTO,

---

\(\ast\) Department of Chemistry, National Taiwan University, Taipei. E-mail: rsliu@ntu.edu.tw

\(\ast\) Department of Physics, National Taiwan Normal University, Taipei. E-mail: sfhu.hu@gmail.com

† Electronic supplementary information (ESI) available: Detailed information on photoluminescence spectra in Fig. S1 and J–V diagram in Fig. S2 and Table S1. See DOI: 10.1039/c0jm00549e
2-2. Synthesis of Eu\(^{3+}\)-modified \(\text{TiO}_2\) nanoparticles

Various amounts of Eu\(_2\text{O}_3\) (Eu\(^{3+}\), where \(x\) represents the molar ratio Eu\(^{3+}/\text{Ti}^{4+}\)) were added to 60 mL water, and the pH value of the solution was tuned to <2 by adding 1 M nitric acid. After vigorous stirring for half an hour, 10 mL tetrabutyl titanate, Ti(OC\(_4\text{H}_9\))\(_4\), was slowly dripped into the solution with vigorous stirring for 1 h. The mixture was heated to 80 °C with magnetic stirring for 10 h and was then transferred into the autoclave at 227 °C for 12 h. Following hydrothermal treatment, a white slurry sample was obtained and then washed repeatedly using ethanol. The white powder was annealed in the atmosphere for 6 h at 500 °C. The final samples were collected for further characterization.

2-3. Preparation of double-layered electrodes for DSSCs

1.125 g ethyl cellulose (5–15 mPa s), 0.875 g ethyl cellulose (30–50 mPa s) and 20 mL ethanol are mixed with vigorous stirring until the mixed solution forms transparent gel. 4 g Eu\(^{3+}\)-\(\text{TiO}_2\) powder, 64.9 g of terpineol and 20 mL of ethanol were added to transparent gel, which was then stirred violently for 90 min. Ethanol and water are removed from mixed solutions using a rotary-evaporator at 40 °C under vacuum for 90 min to yield a white paste. The FTO electrode is coated first with a layer of white paste over an area of 0.16 cm\(^2\) by the doctor blade method and dried at 125 °C for 6 min. The series of thermal treatments is as follows. The paste that coats the FTO is gradually heated under an airflow at 325 °C for 5 min, at 375 °C for 5 min, at 450 °C for 15 min and finally at 500 °C for 15 min. To construct a double-layered electrode, the first layer of the FTO coating is itself coated with Eu\(^{3+}\)-\(\text{TiO}_2\) paste as a second layer by the doctor blade method. The second layer, the FTO coating, is treated by repeating the above thermal procedure. The final Eu\(^{3+}\)-\(\text{TiO}_2\)/Eu\(^{3+}\)-\(\text{TiO}_2\)-coated FTO electrode is immersed in black dye (0.2 mM). A spacing film is placed aside the Pt electrode as a counter electrode. I\(^{-}/\text{I}_3^-\) electrolyte is injected into the space between the Eu\(^{3+}\)-\(\text{TiO}_2\)/Eu\(^{3+}\)-\(\text{TiO}_2\)-coated FTO electrode and the Pt electrode.

2-4. Fabrication of double-layered electrode for use in DSSCs

The Eu\(^{3+}\)-\(\text{TiO}_2\)/Eu\(^{3+}\)-\(\text{TiO}_2\)-coated FTO electrode is immersed in TiCl\(_4\)/EtOH solution at 70 °C for 30 min, and then calcined at 500 °C for 30 min under air flow. The calcined electrode is soaked in black dye (0.2 mM). A spacing film is placed aside the Eu\(^{3+}\)-\(\text{TiO}_2\)/Eu\(^{3+}\)-\(\text{TiO}_2\)-coated TiO\(_2\) electrode, and then combine with the sputtered Pt electrode as a counter electrode. I\(^{-}/\text{I}_3^-\) electrolyte is injected into the space between the Eu\(^{3+}\)-\(\text{TiO}_2\)/Eu\(^{3+}\)-\(\text{TiO}_2\)-coated TiO\(_2\) electrode and the Pt electrode.

3. Results and discussion

Fig. 1a displays the XRD patterns of TiO\(_2\) nanoparticles that have been modified by adding various amounts of Eu\(^{3+}\) with \(x\) from 0.01 to 0.04. The XRD patterns match closely the standard pattern of TiO\(_2\) in the anatase phase, but the diffraction peak of crystalline Eu\(_2\text{O}_3\) and its derivatives cannot be identified. The main diffraction peak is at the same angle (2\(\theta\)) as in the standard pattern, indicating that lattice distance in TiO\(_2\) nanoparticles is constant, according to Bragg’s law (2\(\sin\theta = n\lambda\)). Therefore, the Eu\(^{3+}\) ions cannot be inserted into the lattice of TiO\(_2\) to change the lattice spacing, because of the apparent difference between the radii of Eu\(^{3+}\) ions (1.08 Å) and Ti\(^{4+}\) ions (0.68 Å). In Fig. 1b, the sizes of the TiO\(_2\) nanoparticles, as given by the Scherrer equation, decline from 21.76 nm to 9.78 nm as the amount of Eu\(^{3+}\) ions increases from \(x = 0\) to 0.4. The existence of Eu\(^{3+}\) in the all samples can be proven further by using photoluminescence spectra in Fig. S1 of ESI†. An increase of Eu\(^{3+}\) content on the surface of TiO\(_2\) reveals the decrease of distance among Eu\(^{3+}\). As the distance among Eu\(^{3+}\) is shortened by increasing the amount of Eu\(^{3+}\), the emission light from excited Eu\(^{3+}\) is absorbed easily by neighboring Eu\(^{3+}\), which is ascribed to a concentration quenching effect. In Fig. S1 (ESI†), the intensity of emission increases with increasing amount of Eu\(^{3+}\). However, after the distance between Eu\(^{3+}\) becomes shorter than a critical distance, it decreases owing to concentration quenching effect. Based on the XRD analysis, the Eu\(^{3+}\) ions on the surface of TiO\(_2\) nanoparticles are expected to be inhibited, reducing the number of growth sites for TiO\(_2\) nanoparticles, and causing the size of the TiO\(_2\) nanoparticles to vary with the amount of Eu\(^{3+}\). In the sol–gel reaction, the Ti(OC\(_4\text{H}_9\))\(_4\) species undergo the chemical processes, hydrolysis and condensation, to form crystalline (Ti–O–Ti)\(_n\). Via these processes, Eu\(^{3+}\) forms Eu–O–Ti, modifying the surfaces of the TiO\(_2\) nanoparticles. The results are observed by adding various amounts of Eu\(^{3+}\) from \(x = 0.0075\) to 0.4, to synthesize TiO\(_2\) nanoparticles in various sizes. Hence, Eu\(^{3+}\) ions have an effective
role in inhibiting the growth sites on the surface of TiO₂ nanoparticles, enabling the size of TiO₂ nanoparticles and their modification to be effectively controlled.

Fig. 2 shows the Raman spectra of Eu⁺⁺⁺-modified TiO₂ nanoparticles, to identify the vibration mode of Ti–O bonding. The Raman active vibrational modes for the anatase phase TiO₂ are A₁g + 2B₁g + 3Eg. The absorption peaks at 146, 398, 518 and 641 cm⁻¹ correspond to the vibration modes E_g, A₁g, B₁g and E_g, respectively, which closely match the peaks that are characteristic of Ti–O bonding in anatase. As the x value of Eu⁺⁺⁺ is varied from 0.015 to 0.05, the absorption peak of the E_g mode (416 cm⁻¹) remains the same as those of unmodified TiO₂ nanoparticles (x = 0), indicating that no distortion is observed in the Ti–O symmetry. Previous literature reports no shift of the E_g mode occurs owing to formation of impurity such as Eu₂Ti₂O₇. For our case, all Raman spectra reveal that a pure anatase phase is observed without the presence of the rutile phase or impurities, which is consistent with the result from XRD.

The modification by Eu⁺⁺⁺ on the band gap is investigated using UV-Vis diffuse reflectance spectroscopy (DRS), as shown in Fig. 3a. A strong DRS signal is obtained from unmodified TiO₂ nanoparticles at a wavelength of 323 nm because of the transition of electrons from the O 2p orbital to the Ti 3d orbital. The band gap for optical absorption is defined as the minimum energy equivalent absorption, with BaSO₄ used as a reference (R_ref)¹⁸

\[
F(R_\text{a}) = \frac{(1 - R_a)^2}{2R_a} = \frac{\alpha}{S}
\]

where \(R_a\) represents the ratio \(R_{\text{TiO}_2}/R_{\text{ref}}\), \(\alpha\) and \(S\) denote the absorption coefficient and the scattering coefficient, respectively. Eqn (2) defines the energy-dependence of the absorption coefficient (\(\alpha\)) of TiO₂:\¹⁸

\[
\alpha \propto \frac{(hv - E_\text{g})^\eta}{hv}
\]

where \(v\) is the frequency of the incident photon; \(h\) is the Planck constant, and \(E_\text{g}\) is the optical absorption edge energy. The exponent \(\eta\) is related to whether the band gap associated with the transition of the electron is direct or indirect. Based on eqn (1) and (2), a plot of \(F(R_\text{a})/h^\eta\) as a function of \(hv\) in the absorption edge is linear, and be used to determine the absorption edge energy, which is the band gap. The electronic structure of the material affects the electronic transition between HOMO and LUMO. The transition of electrons with the same momentum as holes can occur directly after the absorption of a photon, while indirect electron transitions are associated with vibrations, which release energy from the crystal lattice as phonons. Herein, the phonon momentum equals the difference between the momentum of the electron and that of the hole, satisfying the conservation of energy and crystal momentum. It obeys well-defined selection rules, in which \(\eta\) values of 1/2, 3/2, 2, and 3, refer to direct-allowed, direct-forbidden, indirect-allowed, and indirect-forbidden transitions, respectively. For TiO₂ material, the value of \(\eta\) is 2, and is used to plot \(F(R_\text{a})/h^\eta\) vs. \(hv\), as shown in Fig. 3b. The band gaps of TiO₂ samples that are modified with various amounts of Eu⁺⁺⁺ complex are obtained from plots of \(F(R_\text{a})/h^\eta\) vs. \(hv\) in Fig. 3c. The band gap shifts to low energy as the amount of Eu⁺⁺⁺ increases. The atomic orbital of Eu⁺⁺⁺ and Ti⁺⁺⁺ with O²⁻ form Ti–O–Eu bonds, such that Eu⁺⁺⁺ modification

Fig. 2 Raman spectra of Eu⁺⁺⁺-modified TiO₂ with x = 0 to 0.05.

Fig. 3 (a) UV-Vis diffuse reflectance spectra of Eu⁺⁺⁺-modified TiO₂ with x = 0 to 0.04, (b) plot of \(F(R_\text{a})/h^\eta\) vs. \(hv\) and (c) x vs. energy gap.
affects the hybridized orbital of TiO₂, reducing the energy of the band gap. Therefore, the size and band gap of Eu⁺⁺⁺-modified TiO₂ nanoparticles can be controlled by adding Eu³⁺. In other words, the size of TiO₂ nanoparticles declines as their specific area increases, supplying the more bonding sites for Eu³⁺ to load on the surface of TiO₂ nanoparticles. Increasing the amount of Eu³⁺ used to modify TiO₂ nanoparticles reduces the energy of the band gap. This effect increases the Eu³⁺ modification of the surface of TiO₂ and is reflected in a substantial shift in the band gap towards lower energy.

The XPS signal from photoelectrons excited from the Ti 2p orbital is obtained to identify chemical state of Ti⁺⁺⁺ in Eu⁺⁺⁺-modified TiO₂ with x = 0 and 0.03, as presented in Fig. 4a. The binding energies of TiO₂ nanoparticles without Eu⁺⁺⁺ modification are 458.3 eV and 464 eV for Ti-2p₃/₂ and Ti-2p₁/₂, respectively. For all samples, the photoelectron signals for Ti are detected at ~458.3 eV and ~464 eV, which indicates the oxidation state of Ti still exists in the form Ti⁺⁺⁺ owing to the lack of reduction of the TiO₂ valence state. However, relative to that of unmodified TiO₂ nanoparticles, the blue shift in the binding energy associated with the Eu⁺⁺⁺₀.03 modification of TiO₂ is 0.2 eV in the form of shifts to 458.5 eV and 464.2 eV for Ti-2p₃/₂ and Ti-2p₁/₂, respectively. Considering the small blue shift, it may arise from the reduction in the density of the electron cloud around Ti atoms by introduction of Eu⁺⁺⁺ modification. Fig. 4b displays an XPS signal from the O 1s orbital for each sample. The increase in the binding energy from 529.7 eV to 529.8 eV reflects the decrease in the density of electron cloud on the O orbital. The decreasing in the density of the electron cloud on the O orbital proceeds in the direction of the expansion of electron cloud from the Ti orbital via the O orbital to the Eu orbital. A comparison with the XRD pattern and Raman spectra may be the evidence for the existence of Eu–O–Ti bonds, indicating that the formation of Ti–O–Eu reduces the density of electron cloud on the surface of TiO₂ nanoparticles rather than insert into TiO₂ lattice.

The structures of the conduction band and the valence band are obtained from the RDS and XPS results (Fig. 5a and 5b), obtained at a low scanning rate using low-energy incident photons. The binding energy is calculated by the equation, \( E_b = h\nu - E_k - \phi \), based on photoelectric effect, where \( E_b \) represents the binding energy, \( h\nu \) is the energy of the incident photon; \( E_k \) denotes the kinetic energy of the photoelectron, and \( \phi \) is the work function. The binding energy of the electron for TiO₂ is obtained by extrapolating the low energy edge of the signal of intensity to the zero line (Fig. 5(a)). The binding energies of Eu⁺⁺⁺₀.03-modified TiO₂ with x = 0 and 0.03 are 2.1 eV and 3.2 eV, respectively. The binding energies of 2.1 eV and 3.2 eV at the onset of the photoelectron’s signal are regarded as the potentials of the electrons localized in the HOMO, using the normal hydrogen electrode (NHE) as the 0 eV reference. Fig. 5(b) depicts the structures of the conduction and valence bands. The conduction and valence bands of the Eu⁺⁺⁺₀.03-modified TiO₂ nanoparticles have higher potentials than those of unmodified TiO₂ nanoparticles, because of the participation of Eu⁺⁺⁺ in the hybridization orbital of TiO₂.

Two double-layered electrodes are constructed. One comprises two layers of unmodified TiO₂ (Type I) and the other consists of unmodified TiO₂ (first layer) and Eu⁺⁺⁺₀.03-modified TiO₂ (second layer) (Type II), as shown in Fig. 6. The performance of DSSCs achieved using these two double layered electrodes is analyzed using IPCE (incident-photon-to-current conversion efficiency) and from the curve of current density (J) against voltage. Fig. 7a displays the measurement of the IPCE for these two electrodes using a series of incident photons with single wavelengths from 350 nm to 1000 nm. The IPCE that is obtained using a type II double-layered electrode reveals that this electrode more efficiently transforms incident photons into current over a wavelength range from 350 nm to 725 nm than is obtained using a type I electrode. Fig. 7b and Table 1 plot and describe the curve of J as a function of voltage, revealing that the current density (J) and...
voltage of the type II electrode are better than those of the type I electrode. Accordingly, the improvement in the current density is caused by an increase in the incident-photon-to-current conversion efficiency in the wavelength range of 350 nm to 725 nm. Using the type II double-layered as an electrode improves the short-circuit current ($J_{sc}$) from 5.65 to 7.06 mA cm$^{-2}$ and increases the open circuit voltage ($V_{oc}$) from 0.66 to 0.71 V. For the double-layered structure, the FFs (fill factors) of these two types of electrode are similar, reaching ~0.7, and are a key parameter in evaluating the performance of solar cells. Therefore, a double-layered type II electrode in DSSCs can be successfully constructed.

Considering the size effect in the secondary layer of two double-layered electrodes, it may cause the efficiency different between them and plays a factor in addition to band effect. Tammy et al.\textsuperscript{24} concentrate on size effect by analyzing the efficiency of a solar cell constructed using TiO$_2$ nanoparticles with 9.8–22.5 nm size. The decrease in efficiency is measured with a decrease of nanoparticle size from 22.5 nm to 15.3 nm owing to a smaller amount of dye absorbed on the surface of the TiO$_2$ layer. If the viewpoint of size effect is only considered, the result is contrary to the small particles with a large specific area for the absorbed dye. Hence, the surface energy needs to be considered as related to the variation in facets of TiO$_2$ nanoparticles after heat treatment. Grant et al.\textsuperscript{25} also observe the same results in size effect and suggest the pore sizes of TiO$_2$ layer play a main role for the access of the sensitizer. Hence, the reduced size of TiO$_2$ nanoparticles causes the efficiency of solar cell to decrease, but in our case the small nanoparticles with ~13 nm are used in fabrication of solar cell as a secondary layer, which improves the efficiency. Therefore, it is estimated that the modified energy band of Eu$^{3+}$ compensates for the disadvantage of small nanoparticle in size effect and further improves the efficiency of solar cells.

Table 1 Results for curve of current density ($J$) vs. potential

<table>
<thead>
<tr>
<th>Type</th>
<th>$V_{oc}$/V</th>
<th>$J_{sc}$/mA cm$^{-2}$</th>
<th>FF</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu$^{3+}$-TiO$_2$/Eu$^{3+}$-TiO$_2$</td>
<td>0.66</td>
<td>5.65</td>
<td>0.70</td>
<td>2.60(8)</td>
</tr>
<tr>
<td>Eu$^{3+}$$_{0.03}$-TiO$_2$/Eu$^{3+}$-TiO$_2$</td>
<td>0.71</td>
<td>7.02</td>
<td>0.68</td>
<td>3.43(2)</td>
</tr>
</tbody>
</table>
as the injection of electron from secondary layer electrode into the inner first layer drives a potential in inner first layer, which forces the excited electron in the inner layer to flow into the FTO. This mechanism yields a high probability of injection of electrons into the FTO layer for the outer secondary and inner first layer, preventing the loss of electrons by their recombination with holes. Fig. 8 presents the energy diagram of the double-layered electrode, according to which, the energy of the conduction band of layer of the Eu^{0.03}-modified TiO_2, −1.04 eV, is higher than that of the first layer of unmodified TiO_2, which has a potential energy of −0.09 eV, yielding a potential difference of 0.95 eV. This 0.95 eV energy barrier not only resists the motion of electrons toward the black dye/electrolyte in the outer layer but also improves electron injection for two layers into FTO, favorably increasing the current density (J) at a given J-voltage (Fig. 7b) and resulting in a highly efficient transformation of incident photons into current, as measured by the IPCE (Fig. 7a).

The open-circuit voltage is the maximum value of different potentials between the hybrid energy level (associated with the photoexcited state of the dye molecules and the conduction band of the Eu_{0.03}-TiO_2/Eu_0-TiO_2 layer) and the HOMO in the redox reaction of the electrolyte (I_3/C_0). The increase in the potential energy of the conduction band of the Eu^{0.03}-modified TiO_2 is responsible for the increase in the open circuit voltage (V_{oc}). Therefore, for the double layer, the modulation of the conduction band not only changes directly the open circuit voltage (V_{oc}) but also promotes the efficiency of injection from the photoexcited state of the dye molecule into the conduction band of the electrode, via Eu^{0.03}-modified TiO_2 as an intermediate state. Furthermore, the increase in the energy of the Eu^{0.03}-modified TiO_2 conduction band to a suitable potential can match the photoexcited state of dye molecules, supporting the forward injection of electrons. The results indicate that the layer of Eu^{0.03}-modified TiO_2 can act as a modulator, improving the operation of the DSSCs, by increasing the efficiency of conversion of the sun’s energy to electricity.

4. Conclusion

The sizes of Eu^{x}-modified TiO_2 nanoparticles are successfully controlled by varying the x value from 0 to 0.04. Eu^{x} ions can be added in the sol-gel method to control the size of TiO_2 nanoparticles by forming Eu-O-Ti bonds, which block the growth sites on the surface of TiO_2 nanoparticles. As the amount of Eu^{x} ions increases, the blocking of the growth sites is increased, resulting in the formation of small nanoparticles. The electronic structure of Eu^{0.03}-modified TiO_2 nanoparticles, including their conduction and valence band, is calculated from the DRS and XPS results, to arrange the double-layered electrode as desired. The energy of the conduction band of the Eu_{0.03}-TiO_2/Eu_0-TiO_2 double layer can be set to reduce the probability of recombination of excited electrons and holes to increase the short-circuit current (I_{SC}) during the operation of the DSSCs. The increase in the open circuit voltage (V_{oc}) from 0.66 to 0.71 V reveals the increase in the difference between the potentials of the hybrid state (conduction band and photoexcited state of dye molecules) and the HOMO in the redox reaction of electrolyte (I_3/C_0) owing to the energy of the conduction band which is increased in the Eu_{0.03}-TiO_2 layer. Finally, the efficiency (η) is clearly improved from 2.20 to 3.43% when the double-layered structure of Eu_{0.03}-TiO_2/Eu_{0.03}-TiO_2 is adopted in the electrode in the DSSCs.

Acknowledgements

The authors would like to thank the National Science Council of Taiwan for financially supporting this research under contract nos. NSC97-2112-M-003-007-MY3 and NSC97-2113-M-002-012-MY3.

References