CHAPTER - VII

7 Reducing Charge Recombination in DSSC Using Ni-doped Titania Nanoparticles on FTO Substrate

Abstract

Controlling the nanocrystalline structure of TiO$_2$ powders is very important for the application to DSSC because the efficiency of DSSC is considerably influenced on the change of the TiO$_2$ nanostructures. Ni-TiO$_2$ powders were synthesized by the conventional acid modified sol–gel method. DSSCs were fabricated using Rhodamine dyes extract using different types of solvent medium and studied the interaction between the dye and TiO$_2$ surface. The X-ray powder diffraction study reveals that all the prepared samples have pure anatase phase tetragonal system. The structural, optical and photovoltaic properties are well discussed in this paper. However, the efficiency of a DSSC using ethanol as extracting solvent was found to be better after being exposed to the simulated sunlight for a short period.
Introduction

Increasing energy demands and concerns over global warming have led to a greater focus on renewable energy sources in recent years. Among all forms of sustainable energy such as wind power, tide energy, geothermal energy, hydrogen energy, and biomass energy, solar energy provides nearly a thousand times of that the sum of all the other energy from which its great potential can be understood. As a main approach to take advantage of solar energy, solar cells are not only clean and resourceful, but they also can be used wherever they are needed. Since the end of last century, the growth of photovoltaic market reaches a high rate of 30% [1].

Figure 7.1 Structure of Solid State DSSC

Nanocrystalline DSSC is emerging as an alternative in the search for new approaches to low cost and more highly efficient solar photovoltaic energy conversion [2, 3]. One important way to
improve the efficiency of DSSC is broadening the absorption spectra of dyes. The investigation and understanding of the performance of a DSSC is quite challenging, being a rather complicated structure. A schematic presentation of the structure of solid state DSSCs is given in Figure 7.1 [4].

The solar spectrum has a large photon flux in the wavelength region 500–1,000 nm, and a good overlap of the optical absorption spectrum of the sensitizer with the solar spectrum is helpful to achieve higher performance of the DSSC [5]. The efficiency of DSSC is determined mainly by the sensitizer used [6]. The heart of the cell consists of a nanocrystalline large band gap metal oxide semiconductor film, with TiO$_2$ being most popular. Transition metal ions are commonly employed as dopants due to their strong absorption of visible light and their similar ionic radius to the parent titanium ion. Nickel is one of transition elements used to modify the titania surface. The effects of Ni on the photocatalytic properties of TiO$_2$ have been investigated by several authors [7, 8]. Ni was selected as dopant because Ni$^{2+}$ has similar radius as Ti$^{4+}$ (the effective ionic radii are 72 pm and 68 pm, respectively). The concentration of the favourable transition metal should be very small. Large concentrations will be detrimental. It has been argued that although impurity energy level would lead to visible light response for wide band gap semiconductor and providing good stoichiometry control and ease of processing [9].

Here, we report our investigation of introducing Ni into TiO$_2$ nanoparticles and the fabrication of DSSCs with TiO$_2$ photoanodes deposited on glass surface by the doctor blade technique with Rhodamine dye. We studied the effect of the polarity of solvents in sensitization process by dissolving the dye in ethanol solvents. It was conformed that the band gap of Ni-doped TiO$_2$ nanoparticles
decreases dramatically and reduced the open-circuit photovoltage. DSSCs based on Ni-doped TiO$_2$ nanopowders improved the cell conversion efficiency from 2.19% to 4.22%.

7.1 Nickel Modified TiO$_2$ Nanoparticles

All chemicals used in this study were reagent-grade without further purification. The pure TiO$_2$ powders (called TiO$_2$-0) were synthesized by acid modified sol gel method. The details are as follows: A 40 $ml$ ethanol (Et-OH) was added drop wise at room temperature to a mixture of 14 $ml$ Ti(OC$_4$H$_9$)$_4$(SA) to obtained solution A. After stirring for 2 hours, a light-yellow transparent solution was formed. After it had gelatinized for 48 h at room temperature, a TiO$_2$ gel with white color was formed. The gel was heated at a rate of 3°C/min and calcined at 450°C for 2 h in a program control oven to get the powdered samples. To prepare Ni-doped TiO$_2$ samples (0.01, 0.03, 0.05 $mol$ %) nickel nitrate were dissolved in 60 $ml$ of deionized water at room temperature, followed by adding 5 $ml$ of glacial acetic acid to obtain solution B. Then, the solution A was added drop-wise into the solution A within 60 min under vigorous stirring. The colour of the calcined powder sample changes from white to pale yellow.

7.2 Results and Discussion

7.2.1 Effects of Surface Morphology

Figure 7.2 shows the FESEM micrographs of the pure and Ni-doped TiO$_2$ nanoparticles prepared by acid modified sol-gel method.
Figure 7.2 FESEM Micrographs TiO$_2$ and Ni-TiO$_2$ Nanopowders

Figure 7.3 XRD Patterns of TiO$_2$ Nanoparticles with Increasing Ni Concentration
It exhibited smooth surface with ordered arrangement with shrinkage of the porous structure and it was conformed that Nickel could be doped into TiO$_2$ lattice successfully by chemical reaction during synthesis. It was found that the doping element did not affect crystalline transformation but it was expected that doping elements would have an affect only on the dye sensitized solar cell photovoltaic properties.

Figure 7.3 shows the XRD patterns of TiO$_2$ with various Ni doping calcined at 450°C. It can be seen that all the samples having pure anatase form. The mean size of the crystallites in samples can be estimated by the FWHM of the XRD peak at $2\theta = 25.3^\circ$ using the Debye-Scherer equation and the crystallite size decreases from 8.62 nm to 7.94 nm with increasing Ni doping from 0% to 0.05 mol %, which may cause by the Ni-O bond distance (1.87 Å) shorter that the Ti-O bond distance (1.94 Å) [10]. These results indicate doping Ni elements can significantly inhibit the growth and increase the specific surface area of nano-TiO$_2$ grains, which is very helpful for the adsorption of dyes on TiO$_2$ and Ni/TiO$_2$ electrodes. Decreasing anatase grain size results in an increase in the total boundary energy for the TiO$_2$ powder.

**7.2.2 Absorption Spectrum Analysis**

Absorption spectroscopies are powerful non-destructive techniques to explore the optical properties of semiconducting nanoparticles. The optical absorption spectra of pure and Ni doped TiO$_2$ nanoparticles are shown in Figure 7.4. The absorbance was expected to depend on several factors, such as bandgap, oxygen deficiency surface roughness and impurity centres. The absorption edge of different samples varies as the concentration of Ni in the
TiO$_2$ nanoparticles varies. In order to calculate the direct band gap we used the Tauc relation

$$\alpha h\nu = A(h\nu - E_g)^n$$  \hspace{1cm} (7.1)

Where $\alpha$ is the absorption coefficient, $A$ is a constant, $n= 1/2$ for direct bandgap semiconductor. An extrapolation of the linear region of a plot of $(\alpha h\nu)^2$ vs $h\nu$ gives the value of the optical band gap $E_g$. The measured bandgap was found to be 3.2 eV for undoped TiO$_2$ nanoparticles. On doping with nickel, the bandgap energy decreases 2.58 eV (0.01 mol %), 2.32 eV (0.03 mol %), 2.08 eV (0.05 mol %), due to the particle size decreases. This is in contrast to the normal phenomenon of quantum confinement. The sensitizer is very stable and has broad range visible light absorption with ethanol solvent medium as shown in Figure 7.5 and the wavelength range between 450 and 600 nm.

Figure 7.4 Absorption Spectra of Pure and Ni-Doped Nanoparticles
Figure 7.5 Absorption Spectra of Rhodamine Dye

7.2.3 I-V Characterization

Photoelectrochemical measurements were carried out using a halogen light source that was focused to one sun at Air Mass (AM) 1.5, at the surface of the cells. The spectral output of the lamp was matched in the region 350 and 800 nm with the aid of a Schott KG-5 sunlight filter so as to reduce the mismatch between the simulated and the true solar spectrum to less than 2%. The current-voltage characteristics of the cells were determined by biasing the cells externally and measured the photocurrents is shown in Figure 7.6 and Table 7.1.
The overall photo conversion efficiency $\eta$ is calculated from the integral photocurrent density ($I_{sc}$), the open circuit photocurrent ($V_{oc}$), the fill factor ($ff$) of the cell, and the intensity of the incident light ($P_{in}$) using the equation,

$$\eta = \frac{V_{oc} \times J_{sc} \times ff}{P_{in}} \times 100\%$$

and $P_{in} = 150 W/cm^2$ at AM 1.5, or under full sunlight and the fill factor ($ff$) is given by the equation $ff = \frac{V_{max} \times J_{max}}{V_{oc} \times J_{sc}}$.

<table>
<thead>
<tr>
<th>Solar cells</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>Efficiency ((\eta) in %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure TiO$_2$</td>
<td>0.54</td>
<td>6.73</td>
<td>2.19</td>
</tr>
<tr>
<td>Ni-TiO$_2$(0.01mol%)</td>
<td>0.57</td>
<td>7.24</td>
<td>2.30</td>
</tr>
<tr>
<td>Ni-TiO$_2$(0.03mol%)</td>
<td>0.63</td>
<td>7.60</td>
<td>3.41</td>
</tr>
<tr>
<td>Ni-TiO$_2$(0.05mol%)</td>
<td>0.64</td>
<td>8.21</td>
<td>4.22</td>
</tr>
</tbody>
</table>
7.3 Conclusion

The photocurrent in the photo-anode of the DSSC composed of aggregate of the anatase phase TiO$_2$ and Ni-doped nanoparticles with Rhodamine dye on the FTO substrate have been analyzed. Conventional photoanode modification can improve the electron injection and suppress electron recombination by forming energy barriers. The optical absorbance spectroscopies reveals that the band gap of the Ni-doped samples show a narrowing effect and the intensity of visible emission increases as the dopant concentration increases. Thus the nickel doping can be used as a method to control the bandgap of the TiO$_2$ nanoparticles.
References