CHAPTER - VIII

8 The Role of Solvents to Improve the DSSC Using Coumarin Dye with TiO$_2$-Ag Doped Nanoparticles

Abstract

In the present study, a pure TiO$_2$ and Ag- doped nanoparticles was prepared via sol-gel method followed by 2h annealed at 450°C in air atmosphere. It’s Structural and optical absorption was investigated by XRD, UV-DRS spectra. The results show that silver doped TiO$_2$ nanoparticles cause the absorption edge shifted to the visible-light region. Pure and silver TiO$_2$ was used as photoanode film developed over Platinum coated FTO as counted electrode with coumarin dye in DMF solvent medium as photo-sensitizer. When Ag–TiO$_2$ was applied in DSSC, the energy conversion efficiency was enhanced significantly compared to that pure TiO$_2$ it was approximately 3.9% with the Coumarin 30 B dye under 100 $mW/cm^2$ of simulated sunlight.
Introduction

Silver-doped titanium dioxide nanoparticles became of current interests because of both their effects on the improvement of photovoltaic effect and photocatalytic activity of TiO$_2$. Kuo et al showed through X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) that silver on TiO$_2$ surface coatings was easily oxidised into silver oxide (Ag$_2$O) and that the addition of silver causes a reduction in photoluminescence intensity as found by photoluminescence (PL) spectroscopy [1].

Dye-sensitized solar cells have been developed since a light-activation mechanism similar to the plant photosynthetic process was applied to solar cells. The working dye sensitized solar cell electrode is made of TCO substrate and wide-gap oxide semiconductor film on which dye molecules are adsorbed [2-4]. Dye serves as the light absorber in DSSC whose properties decide the ability to create electrons and photoelectric conversion efficiency. To obtain high photocurrent, the absorption spectrum of dye should be wide enough. It should also be firmly grafted to the oxide surface and inject the electrons to conduction with a high quantum efficiency. In addition, the dye should also be very stable when exposed to constant light irradiation. Hara and co-workers recently synthesized a series of Coumarin 30 B dye molecules comprised of donor, electron conducting, and anchoring groups for use in solar cell applications [5-7]. The best photovoltaic performance in terms of both conversion yield and long-term stability has so far been achieved with Coumarin 30 B dye.

The aim of this study was to prepare the silver-doped TiO$_2$ nanoparticles and investigated the effects of silver ions on the photovoltaic effect with the polarity of solvents in sensitization
process by dissolving the dye in DMF solvent medium. The structure of TiO$_2$ nanoparticles were investigated in detail and finally the analysis on the photovoltaic performance and configuration of the silver-doped TiO$_2$ could also give some useful information to clarify the doping mechanism of metal ions.

### 8.1 Silver Modified TiO$_2$ Nanoparticle

The Ag-doped TiO$_2$ NPs were prepared by an acid modified sol-gel method. In the first step, Silver nitrate ($0.01\ mol\%$, $0.03\ mol\%$, & $0.05\ mol\%$) were dissolved in $60\ ml$ of deionized water at room temperature, followed by adding $5\ ml$ of glacial acetic acid and in the second step $14\ ml$ titanium isopropoxide was dissolved in $40\ ml$ of anhydrous ethanol with constant stirring. Then, the two solutions were added drop-wise together within $60\ min$ under vigorous stirring. Subsequently, the obtained sol was stirred continuously for $2h$ and aged for $48h$ at room temperature. As-prepared TiO$_2$ gels were dried for $10h$ at $80^\circ C$. The obtained solids were ground and finally calcined at $450^\circ C$ for $2h$ (heating rate = $3^\circ C/min$). The undoped TiO$_2$ nanoparticle was prepared using the same method for comparative purposes.

### 8.2 Results and Discussion

#### 8.2.1 Structure and Morphology Analysis

Figure 8.1 shows the XRD patterns of the TiO$_2$ powers annealed in air at $450^\circ C$. From the graph, both the undoped TiO$_2$ and Ag-doped TiO$_2$ can be assigned to anatase phase with no significant rutile form, according to the standard XRD patterns (JCPDS Patterns No 84-1286). A clear peak broadening in Ag-doped TiO$_2$, versus that for
pure TiO$_2$ and suggested that the Ag-doped TiO$_2$ has a smaller average size than the pure TiO$_2$.

![XRD Patterns of Synthesized Pure and Ag-doped Nanoparticles](image)

**Figure 8.1** XRD Patterns of Synthesized Pure and Ag-doped Nanoparticles

The average crystallite size calculates from the (1 0 1) peak of anatase using Scherrer’s equation, $d = k\lambda/\beta \cos \theta$, where $k$ is the constant (shape factor about 0.9), $\lambda$ the X-ray wavelength, $\beta$ is the Full Width at Half Maximum (FWHM) of the diffraction line and $\theta$ is the diffraction angle. In this case, the average crystallite sizes are 8.62 and 7.8 nm corresponding to the pure TiO$_2$ and Ag-doped TiO$_2$, respectively.
Figure 8.2 shows the FE-SEM micrographs of the pure and Ag-doped TiO$_2$ nanoparticles. It has been observed that the TiO$_2$ nanoparticles annealed at 450°C were almost reveals that the primary particles are quite uniform in size, quite clean and roughly spherical in shape, and that the agglomerates are fused together to form comparatively smaller irregular grains giving rise to highly porous materials which enhancing the photovoltaic performance.

**8.2.2 Optical Properties of Annealed Ag-TiO$_2$ Nanopowders**

UV–vis DRS absorption spectra are used to characterize the light absorption ability of the prepared synthesized nanopowders. Figure 8.3 shows solid-state UV-Vis spectra of several samples prepared
with different mol concentration of silver metal ions. New absorption bands were observed for all the doped samples in the visible range of 400-550 nm in addition to the fundamental absorption edge of TiO$_2$. The bandgap and the wavelength are given in Table 8.1.

![Diffuse Reflectance Spectra of Various Ag-TiO$_2$](image)

**Figure 8.3** Diffuse Reflectance Spectra of Various Ag-TiO$_2$

It is obviously clear that the new absorption bands are mainly due to the doping effect of silver atoms. As a comparison of all references on Silver doped TiO$_2$ nanopowders, UV–vis DRS was not reported repetitively, representing that doping TiO$_2$ with Ag nanopowders could controlled the size and broadening the visible spectrum.
Table 8.1 Wavelength and Bandgap Energy of Synthesized Samples

<table>
<thead>
<tr>
<th>S. No</th>
<th>Sample</th>
<th>Wavelength (λ)</th>
<th>Band Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pure-TiO₂</td>
<td>398</td>
<td>3.2</td>
</tr>
<tr>
<td>2</td>
<td>0.01% Ag-TiO₂</td>
<td>397.66</td>
<td>3.11</td>
</tr>
<tr>
<td>3</td>
<td>0.03% Ag-TiO₂</td>
<td>408.20</td>
<td>3.03</td>
</tr>
<tr>
<td>4</td>
<td>0.04% Ag-TiO₂</td>
<td>427.07</td>
<td>2.90</td>
</tr>
</tbody>
</table>

Figure 8.4 UV Spectra of Coumarin 30 B Dye

The absorption spectrum of Coumarin 30 B dye in DMF solvent medium was obtained using UV-Vis. The wavelength range of spectrum lays between 334nm to 474nm. The related spectrum is shown in Figure 8.4. It originate that, the coumarin 30 B dye have peak absorption at 411nm. From the result, it was understood coumarin 30 B dyes will absorb in the visible region and assume it
must give a better absorption in the photovoltaic performance under illumination conditions.

8.2.3 I-V characterization

![I-V Characteristics of Pure & Ag-doped TiO₂](image)

**Figure 8.5** I-V Characteristics of Pure & Ag-doped TiO₂

Figure 8.5 shows the photovoltaic performance of pure and modified TiO₂ photoelectrodes using Coumarin 30 B dye and Table 8.1 shows the parameters of DSSC. The conversion efficiency of the DSSCs prepared by commercial dye is 3.9% with open-circuit voltage \(V_{oc}\) of 0.78 V and short-circuit current density \(J_{sc}\) of 6.8 mA cm\(^{-2}\).
Table 8.2 $V_{oc}$, $J_{sc}$, FF and $\eta$ of Dye solar cells

<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>0.74</td>
<td>5.7</td>
<td>2.1</td>
</tr>
<tr>
<td>Ag-TiO$_2$ (0.01 mol%)</td>
<td>0.76</td>
<td>6.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Ag-TiO$_2$ (0.03 mol %)</td>
<td>0.76</td>
<td>6.3</td>
<td>3.4</td>
</tr>
<tr>
<td>Ag-TiO$_2$ (0.05 mol %)</td>
<td>0.78</td>
<td>6.8</td>
<td>3.9</td>
</tr>
</tbody>
</table>

8.3 Conclusion

In this summary, we prepared electrodes with TiO$_2$/FTO & Ag-TiO$_2$/FTO via doctor blade method and applied these electrodes to the photoanode of a DSSC. When these photoanode was immersed in the Coumarin 30 B dye with DMF solvent the $J_{sc}$ and $V_{oc}$ values were increased respectively. It was confirmed that the $J_{sc}$ improvement was attributed to the increase in the dye adsorption and enhancement in $V_{oc}$ was caused by the conduction band edge shift of TiO$_2$. Consequently, the conversion efficiency by using Ag-TiO$_2$ with coumarin dye in DMF was a promising material for enhancing the conversion efficiency by simple laboratory preparation method.
References