Chapter 5

Synergistic Effect of AgNps and TiCl$_4$ on Efficiency Enhancement of DSSC

5.1 Introduction

5.2 Experimental details

5.3 Results and discussion

5.4 Conclusions

References

Publication

Synergistic Effect of AgNps and TiCl$_4$ on Efficiency Enhancement of DSSC

5.1 Introduction

Dye-sensitized solar cells (DSSCs) have been widely studied due to several advantages, such as low cost-to-performance ratio, low cost of fabrication, functionality at wide angles and low intensities of incident light, mechanical robustness, and low weight. The structure of DSSC is made of a counter electrode (conductive glass coated with platinum (Pt)), a photo anode (TiO$_2$ porous film on a conductive glass substrate anchored a monolayer of dye) able to absorb dye and an electrolyte of certain organic solvent (containing a redox couple such as iodide/triiodide). When a DSSC is irradiated by sunlight, the electrons of the dye are excited from ground state to excited state by absorbing the photons. The excited electrons are injected into the conduction band of TiO$_2$ porous film and then transferred to the conducting glass through the porous TiO$_2$ film [1]. Dyes are referred to as ‘sensitizers’ because the dye molecules in DSSCs ‘sensitize’ wide-bandgap semiconductors to visible radiation [2].

The efficiency of DSSC may be enhanced by changing the anode material, cathode material, Dye and Electrolyte. In the present work the efficiency enhancement of DSSC was studied by modifying the DSSC anode. The efficiency enhancement of DSSC was also observed by surface plasmon resonance induced by silver nanoparticles (AgNPs) because of increase in absorption coefficient of dye [3–7]. Also TiCl$_4$ pre-treatment on FTO has shown improvement in DSSC parameters it was performed by depositing TiO$_2$ compact layer on the FTO by hydrolysis of TiCl$_4$ aqueous solution which prevents the charge recombination at the interface between FTO and electrolyte, the optimum thickness of compact layer was found to be 25nm, giving 24% increase in the power-conversion efficiency. By TiCl$_4$ post–treatment, TiO$_2$ nanoparticles were formed on the surface of TiO$_2$ films giving enhancement of the surface area and consequently dye adsorption which resulted in the increment of harvested incident light also increase in
photocurrent was observed [1, 8–13]. Further, the incorporation of AgNPs showed light absorption in photo anode active layer of DSSCs by localized surface plasmon excitation and light scattering properties in order to generate more carriers [6, 14–20].

In this chapter, the dye-sensitized solar cells composed of FTO/TiO$_2$/N-719/electrolyte/Pt and FTO/TiO$_2$AgNPs /N-719/electrolyte/Pt are fabricated. Combined strategies for improvement in the efficiency of DSSCs were used. The AgNPs were synthesized by polyol method [7] and results of integration of AgNPs in DSSCs were presented showing a higher photoelectrical performance. The effects of TiCl$_4$ pre and post treatment on DSSCs were also studied to effectively increase the dye absorption on TiO$_2$ anode.

5.2 Experimental details

Analytical grade chemicals were used in the experiment without further purification. Silver nitrate (AgNO$_3$, 99%), polyvinylpyrrolidone (PVP), ethylene glycol (EG), Titanium tetra chloride (TiCl$_4$), Fluorine doped tin oxide glass (FTO), N-719(95%) dye were purchased from Sigma Aldrich. Deionized water was used to prepare aqueous solutions. TiO$_2$ nanoparticles P25 Degussa were purchased from ICE, USA.

5.2.1 Synthesis of AgNPs

To synthesize AgNPs initially 1 mM of polyvinylpyrrolidone (PVP) was added to 5 ml ethylene glycol (EG) and sonicated for 15 min to form a uniform solution, then 1 mM of AgNO$_3$ was added to the solution and heated under constant stirring at a 60˚C in a beaker for 6 h. At this stage, 3 g of sucrose was added to the solution. Consequently the color of the solution turned yellowish indicating the formation of AgNPs. The particles were collected by centrifugation and washed with ethanol and dried in vacuum oven for 48 h. The nanoparticles were characterized by using various methods and were used for the fabrication of DSSC.

5.2.2 Preparation of TiO$_2$ anode

For the fabrication of the plasmonic TiO$_2$ anodes, doctor-blading method was used. For TiO$_2$ layer formation on FTO glass briefly, 0.25 g TiO$_2$ NPs were added to 0.025 g of synthesized AgNPs, the mixture was ground in mortar for 30 min after adding 0.5 ml
acetic acid drop by drop and grinding for another 10 min. Then 4 ml ethanol was added to the composite and sonicated for 30 min subsequently 1.0ml ethyl cellulose solution was added to the composite and the paste was grinded in mortar until it was thick. The prepared paste was applied on FTO of resistance 10Ω/cm² using doctor-blading technique. The TiO₂ photo anodes were annealed starting from 70°C for 10 min by increasing the temperature in steps of 70°C for 10 min duration up to 450°C and kept at this temperature for 30 min.

5.2.3 Preparation of cathode

The DSSC cathode was fabricated by coating platinum on the FTO glass.

5.2.4 TiCl₄ treatment of DSSC anode

To perform the TiCl₄ treatment, the FTO glass was cleaned with ethanol and dipped in 40 mM solution of TiCl₄ for 30 min at 70°C and washed with distilled water immediately after taking out (TiCl₄ pre-treatment). The prepared paste was applied on FTO glass by doctor blading technique and the glass was sintered at 450°C for 30 min and immersed in dye solution for 24 hr. To observe the effect of TiCl₄ post treatment, the dye absorbed anode was again dipped in TiCl₄ solution for 30 min at constant temperature of 70°C.

The prepared photo anodes were immersed in a 0.1mM dye solution of N-719 dye dissolved in ethanol at room temperature for 24 hr. The dye absorbed photo anodes were immediately washed with ethanol and dried naturally in air. To obtain the optimized performance of the DSSC, TiCl₄ pre and post treatments were done on DSSC anode.

The prepared anode and platinum coated cathode after applying silver paste on one side of each electrode were joined together by binding clips slightly displaced leaving the space for electrical connections a drop of iodide electrolyte was poured between the electrodes and the fabricated cell was tested under standard conditions as shown in Figure 5.1.
5.3 Results and discussion

5.3.1 XRD Analysis of TiO$_2$, AgNPs and TiO$_2$AgNPs nanocomposites

X-ray diffraction was used to estimate the crystallite size of AgNPs. The crystallite size ‘D’ of the as-prepared AgNPs was estimated using Debye-Scherer equation:

\[
D = \frac{k \lambda}{\beta \cos \theta}
\]

Where, ‘k’ is the shape factor constant= 0.9, \(\lambda\) is wave length of CuK$_\alpha$ radiation, ‘\(\beta\)’ is full width at half maximum intensity and ‘\(\theta\)’ is diffraction angle in radians of considered diffraction peak. The XRD analysis was performed on a Rigaku Miniflex-II desktop X-ray diffractometer with Cu-K$_\alpha$ irradiation (\(\lambda = 1.5406\ A^\circ\)) over the angular range of 20°-80°.

Figure 5.2 shows the XRD pattern of synthesized AgNPs, TiO$_2$ and TiO$_2$AgNPs nanocomposite. The peaks corresponding with their planes obtained at diffraction angles 37.16°, 43.40°, 63.51° and 76.38° Bragg’s reflection planes represent (111), (200), (220) and (311) face centered cubic (FCC) crystal structure of metallic silver. No extra peak was observed in XRD pattern which showed that no impurity was present in the prepared sample. The sharp and strong peaks reveal that AgNPs are highly oriented and very well matched with standard JCPD Card No (JCPDS 01-1167)[21]. The crystallite size calculated using Debye-Scherer’s formula was found to be 22.1 nm. The XRD patterns of anatase form of TiO$_2$ have a main peak at 2\(\theta = 25.28\) which corresponds to the 101 plane (JCPDS 21-1272). The prominent peaks representing
anatase phase of monocrystalline TiO₂ were observed at 25.3°, 37.8°, 48.0°, 53.9°, 55.0°, 62.7°, 68.7°, 70.3°, and 75.0°. The XRD pattern of nanocomposite show the peaks of both TiO₂NPs as well as AgNPs.

![XRD pattern of pure TiO₂, AgNPs and TiO₂AgNPs nanocomposites](image)

**Figure 5.2. XRD patterns of pure TiO₂, AgNPs and TiO₂AgNPs nanocomposites**

### 5.3.2 FT-IR Spectroscopy TiO₂, AgNPs and TiO₂AgNPs.

FT-IR is widely used quantitative analyses technique in which IR radiations pass through the sample. Some of the IR radiation gets absorbed while others transmitted. The resulting IR spectrum represents fingerprint of the sample with absorption peaks corresponding to the frequency of vibrations between the bonds of the atoms. FT-IR results in clear identification of different type and amount of materials [22].

FT-IR spectra of the prepared samples was recorded in solid phase with PerkinElmer (Spectrum Two) spectrometer in solid phase using KBr pellets technique in the region 400-4000 cm⁻¹. Figure 5.3 shows the FT-IR spectrum of TiO₂, AgNPs and TiO₂AgNPs nanocomposite. Prominent peaks at 3385(O-H) is associated with the stretching vibrations of the –OH group of absorbed water molecules, 2668(C = O) absorption of
CO$_2$ in the air and those at 1635 cm$^{-1}$ are assigned to the bending vibrations of the water molecules [23]. Characteristic broad in the region 400-900 cm$^{-1}$ attributed to Ti-O stretching vibration and O-Ti-O lattice. The peaks at 2115, 1545, and 1265 cm$^{-1}$ are characteristics of stretching and bending vibrations of O-H, C = C and C - O functional groups [24]. Both pure TiO$_2$ and TiO$_2$AgNPs exhibit similar vibration patterns.

![FT-IR patterns of pure TiO$_2$, AgNPs and TiO$_2$AgNPs nanocomposites](image)

**Figure 5.3. FT-IR patterns of pure TiO$_2$, AgNPs and TiO$_2$AgNPs nanocomposites**

### 5.3.3 Scanning Electron microscopy (SEM) of TiO$_2$, AgNPs

The SEM analysis was carried out for synthesized AgNPs. SEM micrographs give the three-dimensional appearance useful for understanding the surface structure of a sample. The morphology of synthesized AgNPs was observed by Scanning Electron Microscope (JEOL, JSM-6510). SEM image of synthesized AgNPs showed that particles are of spherical shape as shown in...
5.3.4 Transmission Electron Microscopy (TEM)

Transmission Electron Microscopic (TEM) analysis was conducted to study the size and the morphology of the synthesized AgNPs. TEM observations were carried out on a high resolution transmission electron microscope (HRTEM), operating at 200 KeV (JEOL 2100F).
TEM image reveals that the AgNPs are uniformly distributed and consist of spherical particles as shown in Figure 5.5. The average particle size estimated by TEM is about 13-23 nm which is in good agreement as calculated from the XRD pattern. It can also be seen from TEM images that some nanoparticles have been agglomerated.

5.3.5 UV-Visible spectroscopy

UV-Visible spectroscopy refers to absorption spectroscopy in the ultraviolet-visible spectral region. In this region of electromagnetic spectrum, molecules undergo electronic transitions. The optical properties of synthesized AgNPs were obtained by PerkinElmer (Lambda -35) UV-Visible spectrophotometer from 250-800 nm.

Figure 5.6 exhibits the surface plasmon resonance peak for AgNPs at 419 nm, which is very close to the value available in literature i.e. around 430 nm [25]. The band gap energies of AgNPs, pure TiO₂, and TiO₂AgNPs nanocomposites from UV–Vis. absorption spectra were calculated using Tauc relation given by:

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

Where, \(E_g\) is the Tauc optical band gap, \(\alpha = 2.303A/d\) is the frequency of incident light \((A: \text{optical density and } d: \text{thickness of the cuvette})\), \(\beta\) is a constant that depends on the width of the localized states in the band gap. The plots of \((\alpha h\nu)^2\) vs \(h\nu\) for AgNPs, TiO₂ and TiO₂AgNPs nanocomposite to calculate the optical band gap are shown in Figure
5.7. The Tauc plot shows band gap of 3.1eV for pure TiO$_2$, 1.6 eV for AgNPs and 2.8 eV for TiO$_2$AgNPs nanocomposite. Thus, it was observed that AgTiO$_2$ nanocomposite leads to reduction in optical gap. The decrease in optical band gap suggested significant reduction of electron-hole recombination, thus improvement in the DSSC efficiency which was attributed to surface plasmon resonance of the Ag nanoparticles[14].

![Figure 5.6. Absorbance spectra of pure TiO$_2$, AgNPs and TiO$_2$AgNPs](image.png)
5.3.6  J-V Characteristics of TiO₂, AgNPs and TiO₂AgNPs DSSC

Photovoltaic characterization of DSSC was performed with a digital source meter (Keithley2400, USA) under standard conditions using solar simulator (Oriel sol 3A, class AAA). Light intensity of 1000W/m², AM 1.5 global at 25°C. The J-V curves were obtained by applying an external bias to the cell and measuring the generated photocurrent.

Figure 5.8 shows the J-V characteristics of the DSSC in different conditions: (i) TiO₂ anode without TiCl₄ treatment (ii) TiO₂ with TiCl₄ pre-treated anode (iii) TiO₂ with both pre and post -treated anode. It was observed that the short circuit current density J_sc was increased with TiCl₄ treatment. Enhanced dye loading and electron transport with the increase in TiCl₄ treatment was found to be the main reasons for enhanced solar cell performance[15]. The short circuit current density J_sc was increased from 6.95 to 12.58 mA/cm² by TiCl₄ treatment with no change in V_oc and fill factor. Further the interfacial adhesion between FTO and the nanoporous TiO₂ layer was also improved by employing the TiO₂ compact layer, which increased the fill factor and J_sc [12]. The DSSCs fabricated with both TiCl₄ pre and post treatment showed enhancement in efficiency.
from 3.29% to 5.61% due to increased photocurrent density. P-V curves exhibited in Figure 5.9 shows the increase in output power density from 3.36 to 5.6 mW/cm².

Figure 5.8. J-V characteristics of the DSSC for TiO₂ with TiCl₄ treatment
Figure 5.9. P-V characteristics of the DSSC for TiO₂ with TiCl₄ treatment

Figure 5.10 shows the J-V characteristics of fabricated DSSC using TiO₂ and TiO₂AgNPs nanocomposites. The characteristics showed improvement in efficiency by the addition of AgNPs. Since the coverage of AgNPs on the anode surface increased the electric field around the particles, enhanced molecular absorbance of the dye and resulted in higher plasmon resonance effect. Consequently, the absorption coefficient of the DSSC and the number of photoelectrons generated was increased by localized surface plasmon of Ag nanoparticles. The best efficiency was obtained using TiO₂AgNPs nanocomposite along with TiCl₄ pre and post treatments. Since $V_{oc}$ depends on the redox potential and the Fermi energy of semiconductors, the intercalation of AgNPs to the TiO₂ layer do no show significant change in $V_{oc}$. [4]
Chapter 5

Synergistic Effect of AgNps and TiCl₄ on Efficiency Enhancement of DSSC

Figure 5.10. J-V characteristics pure TiO₂, AgNPs and TiO₂AgNPs

Figure 5.11. P-V characteristics pure TiO₂, AgNPs and TiO₂AgNPs
The results of Figure 5.10 and Figure 5.11 showed that the enhancement of the dye absorption by the Ag plasmon resonance effect contributes to the photocurrent and indicated improved energy conversion efficiency of DSSC using TiO$_2$AgNPs nanocomposite.

The photoelectric performance of the DSSCs was enhanced due to addition of AgNPs due to decrease in charge-transfer resistance and increase in dye adsorption. The AgNPs induces an impurity level, which caused reduction in the recombination rate of electrons and positively shifted the conduction band edge of TiO$_2$ to match the LUMO level of the dye. The maximum conversion efficiency achieved was 7.3% and the output power density showed increment from 3.34 to 7.34mW/cm$^2$. The cell parameters are presented in Table 5.1. Performance parameters of DSSC for TiO2, AgNPs and TiO2AgNPs

<table>
<thead>
<tr>
<th>S.NO</th>
<th>Anode material</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>Fill Factor</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>TiO$_2$ without TiCl$_4$ treatment</td>
<td>0.69</td>
<td>6.95</td>
<td>0.67</td>
<td>3.36</td>
</tr>
<tr>
<td>2.</td>
<td>TiO$_2$ with TiCl$_4$ pre-treated anode</td>
<td>0.68</td>
<td>11.06</td>
<td>0.69</td>
<td>5.24</td>
</tr>
<tr>
<td>3.</td>
<td>TiO$_2$ with TiCl$_4$ pre and post treated anode</td>
<td>0.68</td>
<td>12.58</td>
<td>0.69</td>
<td>5.61</td>
</tr>
<tr>
<td>4.</td>
<td>TiO$_2$AgNPs without TiCl$_4$ treatment</td>
<td>0.73</td>
<td>9.71</td>
<td>0.74</td>
<td>4.26</td>
</tr>
<tr>
<td>5.</td>
<td>TiO$_2$AgNPs with TiCl$_4$ pre treatment</td>
<td>0.73</td>
<td>10.26</td>
<td>0.74</td>
<td>5.61</td>
</tr>
<tr>
<td>6.</td>
<td>TiO$_2$AgNPs with TiCl$_4$ pre and post treated anode</td>
<td>0.72</td>
<td>13.61</td>
<td>0.74</td>
<td>7.3</td>
</tr>
</tbody>
</table>
5.4 Conclusions

The AgNPs were synthesized successfully by polyol method. From XRD data, it was confirmed that the nanoparticles are in pure form and no impurity peak was observed. SEM images also confirmed that the particles are in spherical shapes with average size of 22.1 nm. TEM image revealed that the sample consist of particles with the average size of 13-23 nm. The short circuit current density $J_{sc}$ was found to increase from 6.95 to 12.58 mA/cm$^2$ by TiCl$_4$ treatment with no change in $V_{oc}$ and fill factor. Due to an increased photocurrent density and efficiency, the DSSCs fabricated with both TiCl$_4$ pre and post treatment showed enhancement in efficiency from 3.29% to 5.61%. P-V curves show the increase in output power density from 3.36 to 5.6 mW/cm$^2$. The fabricated DSSC using AgNPs with both pre and post TiCl$_4$ treated anode appears to have the maximum efficiency as compared to the other cells. Due to effective electron transport and enhanced absorption of dye on TiO$_2$ AgNPs anode surface, the fill factor increases to 0.74 and the maximum conversion efficiency of 7.3% was achieved.
References


synergistic effect of AgNps and TiCl\textsubscript{4} on efficiency enhancement of DSSC.


[18] S.K. Singh, A.D. Borah, J. Borah, TiO2 thin film coated with Silver (Ag) nano-
Chapter 5

Synergistic Effect of AgNps and TiCl₄ on Efficiency Enhancement of DSSC


130