Modified Sol-gel/Impregnation Synthesis of Titanium Dioxide Nanoparticles and Ag-loaded Titanium Dioxide Nanoparticles for Dye-Sensitized Solar Cells Application

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Abstract—TiO_2 nanoparticles and Ag-loaded TiO_2 nanoparticles were synthesized by the modified sol-gel method together with the impregnation method using titanium tetraisopropoxide (TTIP), ethanol (EtOH), ammonia (NH_3) and deionized water as the starting materials. The cellophane membrane was used to control the rate of hydrolysis during sol-gel process. The slow reaction of hydrolysis could produce the small size of TiO_2 nanoparticles. AgNO_3 was used as the Ag precursor for Ag-loaded TiO_2 nanoparticles synthesis. The amount of Ag-loaded was in the range of 0.50–3.00 mol%. The crystal structure and crystallinity of TiO_2 and Ag-loaded TiO_2 nanoparticles were examined by an X-ray diffractometry (XRD). Morphologies and particle sizes of TiO_2 and Ag-loaded TiO_2 nanoparticles were investigated by scanning electron microscopy (SEM) and high resolution transmission electron microscopy (HR-TEM). The chemical composition of TiO_2 and Ag-loaded TiO_2 nanoparticles were examined by energy dispersive X-ray spectrophotometry (EDXS). The specific surface area (SSA_BET) of the samples was investigated by the Brunauer-Emmett-Teller (BET). Anatase phase of TiO_2 was obtained in all samples with an average particle size of 20 nm. The TiO_2 nanoparticles and Ag-loaded TiO_2 nanoparticles have spherical shape. The specific surface area was found to be in the range of 60–100 m²/g. For the enhancement of DSSCs, the dye-sensitized solar cells composed of the ITO/TiO_2/N-719/ electrolyte/Pt and the dye-sensitized solar cells composed of the ITO/Ag-loaded TiO_2/N-719/ electrolyte/Pt were fabricated. TiO_2 films and Ag-loaded TiO_2 films were deposited by using squeegee method using EtOH as a solvent and the films were sintered at 450°C for 30 min before preparation of the cells. Finally, the fabricated cells were studied upon an irradiation of solar light to study the performance and compare the enhancement with the cell fabricated with unloaded TiO_2. The fabricated cell with 1.0 mol% Ag-loaded TiO_2 could enhance the conversion efficiency more than 40% when compared to the fabricated cell with unloaded TiO_2. The performance of the fabricated cells could be enhanced by localized surface plasmon effect and scattering property.

1. Introduction

Titanium dioxide (TiO_2) has several advantages such as chemical stability, nontoxicity, good electrical properties and inexpensive material, therefore it is extensively used in many applications such as photocatalyst, hydrogen production and solar cells [1–4]. Anatase, rutile and brookite are three main crystalline structure of titanium dioxide [3]. Anatase TiO_2 has band gap energy of 3.2 eV of which the absorption thresholds correspond to 380 nm, suggesting that easy for photon-electron transfer under solar light irradiation. Therefore, a mono layer of organic dye molecules cover with covalent bond on anatase TiO_2 film is generally used in the active layer of DSSCs [3, 5].

In 1991, M. Grätzel and O’Regan first introduced a high conversion efficiency DSSCs [6]. After that, many studies on dye-sensitized solar cells (DSSCs) have been reported due to their high efficiency property and low cost of materials [7–14]. To improve light harvesting by light scattering and localized surface plasmon properties of DSSCs, metal nanoparticles were used [10]. Metal nanoparticles have the scattering property which could increase its probability of exciting dye molecule. More electrons to be injected into TiO_2 conduction band due to the increased absorption in the dye. Therefore, the photocurrent of the device could be enhanced [10]. Localized surface plasmon excitation is a collective oscillation of electron in metal particles by incident light excitation. It could enhance the electric field on photoanode of DSSCs in order to increase the optical absorption. Therefore it has been widely used to improve the DSSCs performance [7–10]. Moreover, metal nanoparticle
could perform as electron acceptor from the photo-excited metal oxide. Therefore, electron transfer rate could be improved and the increasing of photocurrent was obtained [7, 15, 16].

Sol-gel method is an interesting method to synthesis TiO$_2$ due to its low cost materials process, high chemical purity, homogeneity and small particle size of the obtained TiO$_2$ particle [17–21]. Sol-gel process consists of 2 main reactions, hydrolysis and condensation [17–26]. In our previous work, we reported the preparation of TiO$_2$ by the modified sol-gel method using cellophane membrane to decrease the diffusion rates of reactants in hydrolysis and condensation steps. The result is the nanosize of TiO$_2$ nanoparticles was obtained [22, 23, 27].

In this research, TiO$_2$ and Ag-loaded TiO$_2$ nanoparticles were synthesized by a modified sol-gel method and the modified sol-gel/ impregnation methods respectively. The obtained particles were used in DSSCs application to enhanced the performance of DSSCs.

II. Experimental

A. Preparation of TiO$_2$ Nanoparticles

Titanium dioxide (TiO$_2$) nanoparticles were synthesized by the modified sol-gel method [32, 33]. Titanium tetraisopropoxide (Ti[OCH(CH$_3$)$_2$]$_4$ (TTIP), Aldrich, England), absolute ethanol (C$_2$H$_5$OH, Merck, Germany) and ammonia (NH$_3$, Merck, Germany) were used as the starting materials for synthesizing TiO$_2$ nanoparticles. Titanium tetraisopropoxide (20 mL) was dissolved in 250 mL absolute ethanol. The mixture of TTIP and absolute ethanol was loaded into a cellophane membrane and suspended for 1 h in a clear solution containing 1:1 ratio of ethanol (95%) and deionized water and 7 mL of ammonia solution (25 %). After the completion of the dialysis process, the suspension was centrifuged at 7500 rpm for 10 min, washed with deionized water and then dried in an oven at 60°C for 24 h. The white powders were then calcined in a furnace at a temperature of 400°C for 3 h.

B. Preparation of Ag-loaded TiO$_2$ Nanoparticles

The impregnation method was used to prepare 0.50–3.0 mol% Ag-loaded TiO$_2$ powders. The solution of (AgNO$_3$), was added into as-prepared TiO$_2$ powders and mixed well. Finally, the obtained powders were dried at 60°C for 24 h and calcined at 400°C for 3 h.

C. Characterization of TiO$_2$ and Ag-loaded TiO$_2$

Nanoparticles

The crystal structure and crystallinity of TiO$_2$ and Ag-loaded TiO$_2$ nanoparticles were examined by an X-ray diffractometry (JDX–3530, JEOL, Japan) using the Ni–filtered monochromatic with CuK$_\alpha$ radiation. The detection range was 15–75° with the step size of 0.10° (2θ/s). Morphologies and particle sizes of TiO$_2$ and Ag-loaded TiO$_2$ nanoparticles were investigated by scanning electron microscopy (SEM, JSM5410-LV, JEOL, Japan) and high resolution transmission electron microscopy (HRTEM, JEM-2010, JEOL, Japan). The chemical composition of TiO$_2$ and Ag-loaded TiO$_2$ nanoparticles were examined by energy dispersive X-ray spectrophotometry (EDXS, ISIS300, Oxford, England). Specific surface area (SSA$_{BET}$) of the samples was investigated by the Brunauer-Emmett-Teller (BET, Micromeritics Tristar 3000).

D. Fabrication of DSSCs and Characterization of the fabricated DSSCs

To compare the performance of DSSCs, TiO$_2$ and Ag-loaded TiO$_2$ nanoparticles were used. The fabrication of DSSCs was described in the previous work [22, 23, 27]. ITO glass substrate with a sheet resistance of 10 Ω/sq was used as an anode. Dish washing liquid solution, water, distilled water and DI water were used for cleaning of ITO substrate. After cleaning process, squeegee technique was used to deposit TiO$_2$ or Ag-loaded TiO$_2$ layers as follows; TiO$_2$ or Ag-loaded TiO$_2$ nanoparticles were dispersed in ethanol. Then, TiO$_2$ or Ag-loaded TiO$_2$ pastes were coated on ITO substrates by squeegee technique. TiO$_2$ or Ag-loaded TiO$_2$ films were then calcined at 450°C for 90 min. To prevent the corrosion of Ag particles by iodine electrolyte, Ag-loaded TiO$_2$ films were immered in 0.001 M 1-octadecanethiol (CH$_3$(CH$_2$)$_{17}$SH, Aldrich, England) for 15 h after calcination step. N-719 (Di-tetrabutylammonium cis-bis(isothiocyanato) bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium(II), Sigma-Aldrich) was used as a photosensitized dye. TiO$_2$ or Ag-loaded TiO$_2$ films were immered in 0.5 mM N-719 dye for 12 h. DSSCs were fabricated as described in the previous work [27]. 0.1 M LiI, 0.05 M I$_2$, 0.6 M (BP, 0.5 M tetrabutyrammonium iodide in acetonitrile were used as electrolyte (for the optimization of the appropriate thickness, only 0.1 M LiI and 0.05 M I$_2$ in acetonitrile was used as electrolyte). Pt film prepared by vacuum evaporation technique was used as the cathode. Photovoltaic properties were studied by irradiating a solar simulator (HAL-C100, 100 W compact xenon light source, ASAHI SPECTRA) to the fabricated DSSCs.

![Fig. 1. XRD patterns of the TiO$_2$ and 1.0 mol% Ag-loaded TiO$_2$ nanoparticles.](image-url)
III. Results and Discussion

A. Synthesis and Characterization of Ag-loaded TiO₂ Nanoparticles

The preparation of the TiO₂ by the modified sol-gel was followed from our previously reported research [32, 33]. And Ag-loaded TiO₂ nanoparticles were prepared by the modified sol-gel method and the modified sol-gel method together with the impregnation method, respectively. Hydrolysis and condensation are main reaction of the sol-gel method [26–31]. As mentioned in our previous work [22, 23, 27], the rates of hydrolysis and condensation affected characteristic of Ag-loaded TiO₂. Cellophane membrane was used to control the hydrolysis and condensation rates in the reaction to obtain the nanosized particles [22, 23, 27]. Impregnation method was used for Ag-loading due to it’s a very simple way which could be synthesized by using inexpensive instruments.

To confirm the structure of TiO₂ and Ag-loaded TiO₂ nanoparticles. XRD patterns were compared with the Joint Committee on Powder Diffraction Standards (JCPDS) Card File No.21–1272 [22, 23, 27]. Fig. 1 shows the XRD patterns of the TiO₂ and 1.0 mol% Ag-loaded TiO₂ nanoparticles. The results of the TiO₂ and 1.0 mol% Ag-loaded TiO₂ nanoparticles were confirmed to be anatase structures according to JCPDS file no. 21–1272 [22, 23, 27]. The Ag-loading might not affect the phase of TiO₂ nanoparticles. The high intensity value of the XRD peaks shows that all of samples have well crystalline structure and the broad peaks at 2θ value of 25.2°.

From the previous reported research [32–34], it was found that high specific surface area of TiO₂ could absorb large amount of dye to produce high device performance. Therefore, specific surface area (SSA) of the samples was investigated by the Brunauer-Emmett-Teller method. The specific surface area of the unloaded TiO₂ and Ag-loaded TiO₂ nanoparticles were found to be in the range of 90–120 m²/g.

Scanning electron microscopy (SEM) was used to investigate the morphology and element chemical compositions as shown in Fig. 2(a). The SEM results showed the rough morphology and the presence of agglomerated nanoparticles. From the EDS mapping mode and EDS spectra as shown in Fig. 2(b), 2(c), 2(d) and 2(e), the chemical compositions of 1.00 at% Ag-loaded TiO₂ showed the characteristic X-ray energy level of titanium, oxygen. The characteristic peaks of Ag were observed to confirm the presence of Ag. Further analysis for the accurate sizes and morphology of the nanoparticles was carried out by HRTEM observation. The average particle diameter of TiO₂ and Ag-loaded TiO₂ nanoparticles were in the range of 10–15 nm based as shown in Fig. 3.

B. Photovoltaic Properties of the Fabricated DSSCs Using TiO₂ and Ag-loaded TiO₂ Nanoparticles

Photovoltaic properties of the fabricated DSSCs using TiO₂ and Ag-loaded TiO₂ nanoparticles were studied to compare the enhancement of Ag-loading to the photovoltaic performance of DSSCs using TiO₂ nanoparticles with various Ag-loading contents. Fig. 4 shows current density versus voltage (J-V) curves of fabricated DSSCs using TiO₂ and 0.5–3.0 at% Ag-loaded TiO₂ nanoparticles. Photovoltaic performances were

![Fig. 3. TEM micrograph of 1.0 mol% Ag-loaded TiO₂ nanoparticles.](image-url)
calculated from these J-V curves as shown in Table 1. The open circuit voltage ($V_{oc}$) is almost constant with all amounts of Ag-loading. This indicates that the Ag-loading to TiO$_2$ does not affect to the Fermi level because the $V_{oc}$ is originated from the energy difference between Fermi level of TiO$_2$ layer and the oxidation/reduction potential of the electrolyte[35].

The results show that the short-circuit current densities ($J_{sc}$) of the fabricated DSSCs with TiO$_2$, 0.5, 1.0, 2.0 and 3.0 at% Ag-loaded TiO$_2$ nanoparticles are 3.11, 4.11, 5.19, 3.81 and 3.53 mA/cm$^2$ corresponding to the efficiency ($\eta$) of 1.75, 2.03, 2.53, 1.87 and 1.83% respectively. These results confirmed that Ag-loading could enhance the photovoltaic performances of DSSCs with the loading amount up to 1.0 at% Ag-loading. Ag could enlarge light absorption in photoanode active layer of DSSCs by localized surface plasmon excitation and light scattering properties in order to generate more carriers [35–39]. However, when the Ag-loading amount was increased to 2.0 at%, the short-circuit current density and the efficiency of the fabricated DSSCs decreased. These effect might be due to the active site was shielded by large amount of Ag leading to low carrier generation and to decrease in DSSCs performance. Moreover, it was suggested that this is because when the amount of Ag loaded on the surface of TiO$_2$ is little, it could not be a very good optical carrier. When the amount of Ag loaded on the surface of TiO$_2$ is more, Ag becomes the recombination center of photo-electron and hole [39].

iv. Conclusion

In this research, the Ag-loaded TiO$_2$ nanoparticles were successfully synthesized by the modified sol–gel method together with the impregnation method. Anatase phase of TiO$_2$ was obtained in all samples with an average particle size of 20 nm. The DSSC was improved by an effect of the Ag-loaded titanium dioxide (Ag-loaded TiO$_2$). The fabricated cell with 1.0 at% Ag-loaded TiO$_2$ could enhance the conversion efficiency more than 40% when compare to the fabricated cell with unloaded TiO$_2$. The performance of the fabricated cells could be enhanced by localized surface plasmon effect and scattering property.

### References


### Table 1. Photovoltaic Performances of Fabricated DSSCs Using TiO$_2$ and 0.5–3.0 mol% Ag-Loaded TiO$_2$ Nanoparticles.

<table>
<thead>
<tr>
<th>Fabricated Cells</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>$\eta$ (%)</th>
<th>FF</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>3.11</td>
<td>0.68</td>
<td>1.75</td>
<td>0.41</td>
</tr>
<tr>
<td>0.50 mol% Ag-TiO$_2$</td>
<td>4.11</td>
<td>0.66</td>
<td>2.03</td>
<td>0.37</td>
</tr>
<tr>
<td>1.0 mol% Ag-TiO$_2$</td>
<td>5.19</td>
<td>0.70</td>
<td>2.53</td>
<td>0.35</td>
</tr>
<tr>
<td>2.0 mol% Ag-TiO$_2$</td>
<td>3.81</td>
<td>0.66</td>
<td>1.87</td>
<td>0.37</td>
</tr>
<tr>
<td>3.0 mol% Ag-TiO$_2$</td>
<td>3.53</td>
<td>0.66</td>
<td>1.83</td>
<td>0.39</td>
</tr>
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