Fabrication of TiO$_2$-Ag composites for working electrode of dye-sensitized solar cells


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**Abstract.** A solar cell is a device that can convert solar energy into electrical energy. The third generation of solar cells is Dye-Sensitized Solar Cells (DSSC). Typically, DSSC consists of a working electrode (semiconductive metal oxide), a photosensitizer, an electrolyte, and a counter electrode (platinum or carbon electrode). Among the components, a working electrode is one of the crucial components to control the electrochemical performance. This study examines variations in Ag composition in TiO$_2$-Ag composites against efficiency using two materials and fabrication methods. First, using the solid-state method, TiO$_2$-Ag composites were fabricated from Ag paste and TiO$_2$ paste. The highest efficiency results were achieved at TiO$_2$ N-RT + Ag 1%. The efficiency increased from 1.05% to 1.51% compared to TiO$_2$ without Ag doping. Second, using the solvothermal method, TiO$_2$-Ag composites were fabricated from AgNO$_3$ and TiO$_2$ particles. The highest efficiency results were obtained at TiO$_2$ NP + Ag 0.75%. The efficiency increased from 0.82% to 1.07% compared to TiO$_2$ without Ag doping. Furthermore, the material with the best efficiency was characterized using FTIR, XRD, and SEM to identify the material’s functional groups, phases, and morphology, respectively.

**1 Introduction**

Dye-Sensitized Solar Cell (DSSC) is an important advance in third-generation solar cell technology that can convert solar energy into electrical energy. Its beginnings can be attributed to the pioneering efforts of the esteemed Gratzel and his colleagues, who introduced this remarkable innovation in 1991. Typically, DSSC consists of a working electrode (photoanode), a photosensitizer, an electrolyte (triiodide/iodide (I$_3^-$/I$^-$) redox couple solution), and a counter electrode (platinum or carbon electrode). DSSC shows similarities to plant photosynthesis[1].

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In this interesting phenomenon, photosensitizers inside cells absorb incident light as photons. As a result, electrons residing within the dye are stimulated and raised to higher energy levels, specifically the conduction band of the photoanode. Furthermore, these electrons will diffuse towards the back contact, which continues to the counter electrode through the external circuit. At the counter electrode, electrons are involved in reducing $I_3^-$ to $I^-$, thereby facilitating the process of regenerating or restoring the dye to its ground state. Simultaneously, $I^-$ undergoes oxidation, turning into $I_3^-$ [2]. The operational dynamics of a DSSC depend on the important function of the photoanode within its framework. A photoanode that exhibits optimal efficiency necessitates fulfilling various criteria, including a substantial surface area to facilitate extensive absorption, enhanced scattering capabilities to maximize light harvesting, and appropriate pore size to facilitate proper diffusion[3]. Among the various transition metal oxides, titanium dioxide (TiO$_2$) is widely regarded as the most proficient material for utilization as a photoanode due to its ability to meet all the aforementioned criteria. Nevertheless, TiO$_2$ may exhibit certain drawbacks, notably the limited electron mobility[4]. Hence, doping TiO$_2$ with substances that augment electron mobility, such as transition metal ions or carbon-based materials, can potentially enhance the film’s charge transport and electron mobility. The strategic incorporation of transition metal ions into TiO$_2$ can effectively alter the inherent band structure, thereby enhancing the processes of charge separation and transport[5]. Among the transition metals that have been reported, silver (Ag)-doped TiO$_2$ shows outstanding performance. In their recent study, Khojasteh et al. (2021) employed a combination of TTIP and 2-propanol within acetic acid solvents as a precursor for TiO$_2$ and AgNO$_3$ via a hydrothermal process, resulting in a DSSC performance efficiency of 5.13%[6]. Khan et al., 2021 and Rajintha et al., 2020 succeeded in doping TiO$_2$ with Ag using the sol-gel method and obtained 29% and 41% higher efficiency than TiO$_2$ without doping, respectively[3,7]. Some researchers also synthesize Ag-doped TiO$_2$ Nanofibers in their DSSC studies using the electrospinning method[4,8,9].

Here, we investigate variations in Ag composition in TiO$_2$-Ag composites with two distinct materials and fabrication methods. In the first method, TiO$_2$-Ag composite was prepared using the solid-state method from commercial Ag and TiO$_2$ paste. The second method, TiO$_2$-Ag composite was prepared from AgNO$_3$ and TiO$_2$ particles using the solvothermal method. The solvothermal method offers several advantages for DSSCs, including fine particle size and unique physical properties. This advantage contributes to improved DSSC performance as it can increase the surface area of TiO$_2$, enabling more efficient light absorption and electron transfer[10].

2 Experimental

2.1 Solid-State Method

The working electrode was prepared by weighing 0.5 g of TiO$_2$ NR-T paste (Greatcell Solar Materials Pty Ltd) and 0.005 g of Ag paste (Solaronix SA) for TiO$_2$ NR-T + Ag 1% sample. For TiO$_2$ NR-T + Ag 2%, TiO$_2$ NR-T + Ag 3%, and TiO$_2$ NR-T + Ag 4% samples, 0.01 g, 0.015 g, and 0.02 g Ag paste were added to 0.5 g TiO$_2$ NR-T paste, respectively. Next, TiO$_2$ NR-T paste and Ag paste were mixed with 1 mL of ethanol (PT Smart-lab Indonesia) in the beaker glass using a magnetic stirrer for 15 minutes. Then the paste was deposited on the FTO glass (Greatcell Solar Materials Pty Ltd). As a comparison, the TiO$_2$ NR-T paste was directly deposited on the FTO glass for the sample without Ag doping.
2.2 Solvothermal Method

TiO$_2$ NP + Ag 1% sample was prepared by mixing 0.5 g TiO$_2$ P25 (Merck) and 5 mg AgNO$_3$ (Merck) in 100 mL ethanol for 30 minutes. Other sample variations were prepared according to the mass ratio of AgNO$_3$ to TiO$_2$ P25. Then, the mixture was sonicated for 10 minutes and was heated in an autoclave at 160°C for 16 hours. After that, the solids were filtered and washed using distilled-water (PT Citosa Kamila Prima). The solid was heated at 80°C for 7 hours using a vacuum oven. TiO$_2$ P25 and AgNO$_3$ pastes were prepared by mixing 2 g of solid with 5 mL of distilled-water, 1 mL of acetic acid (Merck) and 1 mL of Triton X100 (Merck). Next, the paste was applied to the FTO glass. As a comparison, TiO$_2$ P25 (TiO$_2$ NP) without the addition of AgNO$_3$ were also processed by this method.

2.3 DSSC Fabrication

Pre-treatment FTO glass: The FTO glass used was 2 cm x 2 cm with an active layer of 0.7 cm x 0.7 cm. FTO glass for the counter electrode was perforated. Then, the FTO glass was immersed in a beaker containing alcohol and sonicated using an ultrasonic cleaner for 10 minutes. The sonicated FTO glass was immersed in 40 mM TiCl$_4$ (Merck) solution and heated on a hotplate at 70°C for 30 minutes. Then the FTO glass was washed using ethanol and heated on a hotplate at 450°C for 30 minutes.

Counter electrode: The counter electrode was prepared by depositing platinum (Pt) paste (Dyenamo AB) on the FTO glass. Followed by an annealing process using a furnace at a temperature of 450°C for 45 minutes.

Working electrode: Paste from solid-state or solvothermal method was deposited onto FTO glass using the doctor blade method. The layer was heated in a furnace at 450°C for 45 minutes. Then, the layer was soaked in 40 mM TiCl$_4$ solution and heated on a hotplate at 70°C for 30 minutes. Furthermore, the layer was washed using ethanol and heated on a hotplate. The layer was heated again on the hotplate at 450°C for 30 minutes. The layer was soaked in 0.75 mM N719 dye solution (Solaronix SA) for 24 hours.

Assembly DSSC: DSSC was assembled by stacking the working electrode, Surlyn (Solaronix SA), and counter electrode. Then, it was heated in a hot press at a temperature of 250°C for 6 minutes. After that, the Mosalyte electrolyte (Solaronix SA) was injected through the hole on the counter electrode and covered by silicone rubber.

2.4 Characterization Techniques

Several characterizations were carried out to determine the chemical, physical, and electrochemical properties of the sample. A photovoltaic test was carried out to determine the electrochemical properties of the sample with a solar simulator (1000 W.m$^{-2}$ and AM 1.5) and Keithley 2400. The test results are in the form of a voltage-current density curve. Then, an X-Ray Diffraction (XRD) test was performed to analyze the structure of the crystalline material. The XRD test (D2-Phaser Bruker, Germany) was carried out in the 0-20 range 10-80$^\circ$ with $\lambda = 1.5406$ using CuK$\alpha$ radiation. Fourier Transform Infrared Spectroscopy (FTIR) analysis (IRSpirit, Shimadzu, Japan) was performed to identify and analyze functional group of organic and inorganic materials based on their infrared absorption properties. The FTIR analysis was carried out in the wavenumber 400-4000 cm$^{-1}$ at room temperature. Scanning Electron Microscopy-Energy Dispersive X-ray (SEM-EDX) (JCM 7000, JEOL) for imaging and analyzing sample surface morphology and elemental composition.
3 Discussion

3.1 J-V Characterization

The photovoltaic performance of several DSSC samples prepared using varying amounts of silver (Ag) and using two different methods has been investigated. In order to conduct a comprehensive analysis of the photovoltaic performance of DSSC, a series of photovoltaic tests were conducted on various samples under standard test conditions, specifically at an irradiance of 1000 W.m\(^{-2}\) and an air mass of 1.5 (AM 1.5). The findings derived from the photovoltaic tests are visually depicted in Fig. 1 and quantitatively summarized in Table 1. The values of short circuit photocurrent density (J\(_{sc}\)), open circuit voltage (V\(_{oc}\)), charge factor (FF), and efficiency extracted from the solar cell curves are presented in Table 1.

![J-V curve of DSSC fabricated from (a) solid-state and (b) solvothermal method.](image)

Based on Figure 1 and Table 1, TiO\(_2\) NR-T + Ag 1% gave the best performance with values of J\(_{sc}\), V\(_{oc}\), FF, and efficiency of 4.458 mA.cm\(^{-2}\), 0.669 V, 0.507 and 1.511%, respectively, for the solid-state method. While TiO\(_2\) NP + Ag 0.75% gave the best performance with values of J\(_{sc}\), V\(_{oc}\), FF, and efficiency of 3.514 mA.cm\(^{-2}\), 0.574 V, 0.532, and 1.071%, respectively, for the solvothermal method. The V\(_{oc}\) values of TiO\(_2\) NR-T + Ag 1% and TiO\(_2\) NP + Ag 0.75% against TiO\(_2\) NR-T and TiO\(_2\) NP showed a slight increase. The experimental results also show that the addition of Ag causes an increase in J\(_{sc}\), resulting in more efficient transport of charge carriers[11]. This increase in the J\(_{sc}\) value can be attributed to the rise in optical absorption of the incident photons. The presence of Ag in the photoanode effectively reduces the length of the electron transport path, thereby facilitating the efficient transfer of electrons from the TiO\(_2\) layer to the substrate. Therefore, this phenomenon can be attributed to the decreased resistance in the TiO\(_2\)-Ag composite[12]. As a result, the overall efficiency of the system is improved.

In contrast, increasing the composition to more than 1% Ag for the TiO\(_2\)-Ag composite eventually led to a decrease in the conversion efficiency. This phenomenon can be attributed to the correlation between the concentration of Ag and the shielding of the following active site. Accumulating large amounts of Ag reduces carrier generation and overall photo performance[12]. In addition, higher Ag loading can lead to unbound or excess Ag in the composite material. This excess Ag has the potential to undergo oxidation, forming Ag(I) ions and further eroding the redox electrolyte[13]. Ag oxidation will serve as a new
recombination center, facilitating the interaction between photoelectrons and holes, thereby causing a decrease in the number of charge carriers. Thus, resulting in reduction of Jsc and Voc and consequently decrease in the overall conversion efficiency of the DSSC.

### Table 1. Photovoltaic parameters of DSSCs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Jsc (mA·cm⁻²)</th>
<th>Voc (V)</th>
<th>FF</th>
<th>Efficiency (%)</th>
</tr>
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<tbody>
<tr>
<td>TiO₂ NR-T</td>
<td>3.458</td>
<td>0.582</td>
<td>0.520</td>
<td>1.047</td>
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<tr>
<td>TiO₂ NR-T + Ag 1%</td>
<td>4.458</td>
<td>0.669</td>
<td>0.507</td>
<td>1.511</td>
</tr>
<tr>
<td>TiO₂ NR-T + Ag 2%</td>
<td>4.190</td>
<td>0.620</td>
<td>0.545</td>
<td>1.415</td>
</tr>
<tr>
<td>TiO₂ NR-T + Ag 3%</td>
<td>3.532</td>
<td>0.611</td>
<td>0.581</td>
<td>1.254</td>
</tr>
<tr>
<td>TiO₂ NR-T + Ag 4%</td>
<td>3.014</td>
<td>0.581</td>
<td>0.482</td>
<td>0.844</td>
</tr>
<tr>
<td>TiO₂ NP</td>
<td>2.663</td>
<td>0.572</td>
<td>0.537</td>
<td>0.818</td>
</tr>
<tr>
<td>TiO₂ NP + Ag 0.25%</td>
<td>2.154</td>
<td>0.479</td>
<td>0.551</td>
<td>0.568</td>
</tr>
<tr>
<td>TiO₂ NP + Ag 0.50%</td>
<td>2.597</td>
<td>0.506</td>
<td>0.537</td>
<td>0.706</td>
</tr>
<tr>
<td>TiO₂ NP + Ag 0.75%</td>
<td>3.514</td>
<td>0.574</td>
<td>0.532</td>
<td>1.071</td>
</tr>
<tr>
<td>TiO₂ NP + Ag 1%</td>
<td>2.685</td>
<td>0.530</td>
<td>0.458</td>
<td>0.651</td>
</tr>
<tr>
<td>TiO₂ NP + Ag 2%</td>
<td>1.905</td>
<td>0.552</td>
<td>0.566</td>
<td>0.595</td>
</tr>
<tr>
<td>TiO₂ NP + Ag 3%</td>
<td>1.957</td>
<td>0.559</td>
<td>0.535</td>
<td>0.586</td>
</tr>
</tbody>
</table>

3.2 XRD Characterization

Based on the photovoltaic performance, the highest efficiency was achieved at TiO₂ NR-T + Ag 1% for the solid-state method and TiO₂ NP + Ag 0.75% for the solvothermal method. XRD characterization was carried out to identify the crystalline phases. The XRD patterns of TiO₂ NR-T + Ag 1% and TiO₂ NP + Ag 0.75% were shown in Fig. 2. All samples have peaks that match the crystallographic structure of TiO₂ (anatase) with JPCDS No. 21-1272. The degree of crystalline order was indicated by the strongest intensity peak at 2θ = 25.3° (101). Furthermore, the characteristic peak for Ag did not show in the XRD pattern. It indicated that the addition of Ag did not affect the TiO₂ (anatase) phase due to low Ag concentration[14,15].

The size of nanoparticles was estimated using Debye-Scherer’s equation as follows:

\[
d = \frac{\kappa \lambda}{\beta \cos \theta}
\]

where d is the size of nanoparticles in nm, k is the shape factor of 0.9, λ is the X-ray wavelength of 1.5406 Å, θ is the degree of the Bragg angle, and β is the full width at half maximum (FWHM) of the peak[16].

The size of nanoparticles were 14.01 nm and 13.62 nm for TiO₂ NR-T and TiO₂ NR-T + Ag 1%, respectively. In comparison with samples of the solid-state method, the size of
nanoparticles obtained by the solvothermal method was larger, namely 57.71 nm and 50.02 nm for TiO$_2$ NP and TiO$_2$ NP + Ag 0.75%, respectively. The size of nanoparticles was related to the FWHM value. At higher the FWHM value, the size of nanoparticles was smaller. The FWHM values 0.581, 0.597, 0.141, 0.162 for TiO$_2$ NR-T, TiO$_2$ NR-T + Ag 1%, TiO$_2$ NP and TiO$_2$ NP + Ag 0.75%, respectively. The FWHM value was higher in the sample with the addition of Ag which affected the dynamics of grain growth. In addition, the difference in the size of nanoparticles is due to the effect of heat treatment[6].

![XRD pattern of particles fabricated from (a) solid-state and (b) solvothermal method.](image)

Fig. 2. XRD pattern of particles fabricated from (a) solid-state and (b) solvothermal method.

3.3 FTIR Characterization

![FTIR spectra of particles fabricated from (a) solid-state and (b) solvothermal method.](image)

Fig. 3. FTIR spectra of particles fabricated from (a) solid-state and (b) solvothermal method.

The FTIR spectra of TiO$_2$ and TiO$_2$ + Ag composites in the range of 400-4000 cm$^{-1}$ were indicated in Fig. 3. It can be clearly seen from FTIR spectra that the wide absorption band at
422-428 cm$^{-1}$ represents Ti-O-Ti bonding[17]. The broad peak around 1632-1649 cm$^{-1}$ corresponds to the presence of the bending vibration of hydroxyl group, absorbed or free water. The broad peak at 3000-3500 cm$^{-1}$ in TiO$_2$ ascribe to stretching vibrations of hydroxyl group that are linked to titanium atoms (Ti-OH) [5,18,19]. The absorbed or free water content in TiO$_2$ is affected by the presence of water vapor on the surface in open air. No other peaks were detected. This indicates no impurities in the TiO$_2$ and TiO$_2$ + Ag particles. Additionally, the addition of Ag did not change the FTIR spectra.

3.4 SEM Characterization

Fig. 4 illustrates the surface morphology of TiO$_2$ NR-T, TiO$_2$ NR-T + Ag 1%, TiO$_2$ NP, and TiO$_2$ NP + Ag 0.75% layer at magnification of x1000. TiO$_2$ NR-T layer had a smooth surface (Fig. 4(a)). As seen, while the surface of the TiO$_2$ NR-T + Ag 1% layer had a slightly rough surface (Fig. 4(b)). There was some agglomeration on the TiO$_2$ NP layer (Fig. 4(c)) and with the addition of Ag nanoparticles the amount of agglomerates increased (Fig. 4(d)).

![Fig. 4. SEM image of (a) TiO$_2$ NR-T, (b) TiO$_2$ NR-T + Ag 1%, (c) TiO$_2$ NP, and (d) TiO$_2$ NP + Ag 0.75% layer at x1000 magnification.](image)

Compared between the layers from the solid-state method (Fig. 4 (a) and Fig. 4 (b)) and the solvothermal method (Fig. 4 (c) and Fig. 4 (d)), agglomerates were clearly visible on the surface of the layer from the solvothermal method. In addition, crack formation was found on the surface of the layer from the solvothermal method as seen in Fig. 5. Crack in the layer will degrade the electronic connectivity and further lead to bad photovoltaic performance.
According to EDX characterization in Table 2, the composite is composed of Ti, O and Ag which confirms the absence of any other impurities. TiO$_2$ NR-T + Ag 1% particles have a mass and atomic percentage of Ag higher than TiO$_2$ NP + Ag 0.75%. In this study, the composition of Ag on TiO$_2$ NR-T + Ag 1% was three times the requirement due to weighing error. However, the composition of Ag on TiO$_2$ NP + Ag 0.75% was less. It is possible that some of the particles were carried away during the washing process.

**Table 2.** Mass and atomic percentages of TiO$_2$ NR-T + Ag 1% and TiO$_2$ NP + Ag 0.75%

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass (%)</th>
<th>Atom (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ti</td>
<td>O</td>
</tr>
<tr>
<td>TiO$_2$ NR-T + Ag 1%</td>
<td>59.91</td>
<td>36.86</td>
</tr>
<tr>
<td>TiO$_2$ NP + Ag 0.75%</td>
<td>61.80</td>
<td>37.51</td>
</tr>
</tbody>
</table>

**4 Conclusion**

In summary, we have successfully fabricated TiO$_2$-Ag composites using two distinct methods, solid-state method and solvothermal method. Ag deposition on TiO$_2$ matrix can facilitate the efficient transfer of electrons. Hence, TiO$_2$ NR-T + Ag 1% (efficiency = 1.511%) and TiO$_2$ NP + Ag 0.75% (efficiency = 1.071%) had better photovoltaic performance compared to a pure TiO$_2$ NR-T (efficiency = 1.047%) and TiO$_2$ NP (efficiency = 0.818%). In addition, the working electrode layer from the solvothermal method was cracked resulting in lower photovoltaic performance than the sample from the solid-state method.

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References