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Article

Preparations and Analyses of Titanium Dioxide and Silver Nanowire Composite Thin Films

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Abstract: The dye-sensitized solar cell (DSSC) is the third generation of polycrystalline silicon solar cells, offering advantages such as low cost, simple manufacturing processes, and significant development potential. Compared with traditional silicon-based solar cells, DSSCs have lower production costs and can be fabricated on flexible substrates, making them appropriate for a wide range of applications, including wearable devices and building-integrated photovoltaics (BIPV). Silver nanowires possess excellent surface plasmon resonance, high conductivity, and low resistance, enabling rapid electron transfer. These characteristics make silver nanowires ideal for creating composite materials for photoanodes. Silver nanowires can significantly enhance the photoelectric conversion efficiency of solar cells, thereby improving their overall performance. We incorporated different concentrations of silver nanowires into titanium dioxide (TiO2) slurry and coated it onto indium tin oxide (ITO) conductive glass substrates using the doctor blade method. After coating, the samples underwent a molding process to achieve an average film thickness of approximately 10 micrometers. Subsequently, the samples were annealed at a high temperature. The annealing process improved the crystallinity and conductivity of the films while eliminating stresses and defects generated during fabrication. This fabrication method is simple and controllable for large-scale production. The effects of annealing on the properties of TiO_2 films with added silver nanowires were explored by measuring surface morphology, crystalline structure, conductivity, and photoelectric conversion efficiency. The research results provide theoretical foundations for optimizing the manufacturing processes of DSSCs and broadening applications.

Keywords: Dye-sensitized solar cells, Silver nanowires, Titanium dioxide, Doctor blade method, Molding

1. Introduction

Solar energy is inexhaustible. If we can effectively harness this energy, traditional energy sources can be replaced, and the energy crisis and the issue of non-renewable resources can be solved with environmental problems mitigated. Among the various green energy solutions, solar cells are the most promising owing to rapidly developing technology. The energy from the Sun reaching Earth each year is approximately 3,850,000 exajoules. More energy reaches the Earth than the total global energy consumption yearly. If we capture and convert solar energy into electricity efficiently, it effectively solves the problem of energy shortages. Therefore, solar cells have significant research and development potential as green energy.

Dye-sensitized solar cells (DSSCs) are used widely due to their low manufacturing costs. The fabrication of the DCCS does not require cleanrooms [1–4]. They are less affected by sunlight incident angles and temperature. Additionally, DSSCs are transparent and can even be flexible, making them appropriate for a variety of applications as they generate electricity from indoor light sources. These characteristics allow DSSCs to be commercially applied as promising solar cells in various applications.

The localized surface plasmon resonance (LSPR) of silver nanomaterials is significantly influenced by the shape, size, and thickness of the nanostructures [5]. When a light of a specific wavelength irradiates a metallic surface or metallic nanostructures, surface plasmon resonance occurs, generating an electromagnetic field that decays exponentially from the surface into the surrounding medium. This decaying wave can be directly utilized to effectively concentrate emitted photons, thereby exciting molecules close to the metallic nanomaterials. This mechanism enhances the quantum yield and improves the solar energy conversion efficiency of DSSCs. LSPR by altering the nanostructure's physical properties opens up numerous possibilities for optimizing the performance of DSSCs. By precisely tuning the shape, size, and thickness of silver nanomaterials, the resonance effect is maximized, and the efficiency of photon capture and utilization is increased. This optimization process is crucial because

it directly affects the amount of harvested light and its conversion to electrical energy. Furthermore, the enhancement of quantum yield through the excitation of nearby molecules contributes to an efficient charge separation and transfer process of the DSSC. This results in higher photocurrent and overall better performance. Consequently, the application of LSPR in nanomaterials offers benefits in advancing solar energy technologies [6].

We incorporated silver nanowires into titanium dioxide (TiO_2) paste to create a composite photoanode layer. Silver nanowires exhibit excellent electronic transport properties, thermal conductivity, low electrical resistance, conductivity, and reflectivity. These characteristics allow for efficient electron transport and prolong electron lifetime, thereby suppressing electron-hole recombination and enhancing the overall photoelectric conversion efficiency. Silver nanowires are particularly appropriate for DSSCs as they increase the current generated by the photoanode and improve the photovoltaic performance. Silver nanowires can be used to enhance the performance of DSSCs, as they offer better electron mobility and reduce energy losses. By optimizing the concentration and distribution of silver nanowires in the TiO_2 matrix, the efficiency can be maximized. The high reflectivity of the nanowires also enables light scattering, which increases the absorption of photons and boosts the efficiency of the solar cells. By exploring various parameters such as the size and aspect ratio of the silver nanowires, the best performance of DSSCs was confirmed in this study.

2. Materials and Methods

TiO_2 powder (P25) was added to two glass bottles. The first bottle was used to prepare a pure titanium dioxide slurry by adding tert-Butanol and deionized water in a 2:1 ratio. The second bottle contained a composite slurry with silver nanowires and tert-butanol was added into it. Silver nanowires and deionized water were added in a 2:1 ratio. The mixtures were then stirred uniformly for 24 h for thorough mixing, ensuring that the TiO_2 particles and AgNWs were evenly dispersed throughout the slurry. The concentration of the titanium dioxide slurry was 10 wt%, while the concentrations of silver nanowires were 0.01, 0.03, 0.05, 0.07 0.09, and 0.11 wt%. The process of producing the slurries is critical for ensuring the homogeneous distribution of the TiO_2 and AgNWs. Tert-Butanol was used to stabilize the dispersions and prevent agglomeration of the particles to maintain consistent properties in the final products. The 24-hour stirring period allows.

Electrodes were prepared by depositing a metallic film of approximately 10 nm onto indium tin oxide (ITO) transparent conductive glass using a gold plating machine at 10 mA for 40 s. This metallic film serves as the cathode in DSSCs. In addition to conducting current, it acts as a catalyst for the $I^-/I3^-$ redox couple, reducing I^- ions to I_3^- ions. Additionally, it reflects incident light to the working electrode for multiple excitations. Currently, the most commonly used counter electrode material is platinum (Pt) due to its low resistance, low reactivity, excellent catalytic properties, high oxidation potential, and minimized unwanted reactions. Pt is also stable and resists corrosion from the $I^-/I3^-$ electrolyte for extended periods, enhancing the operational lifespan of the cells. This makes Pt appropriate for DSSCs. The composite film of silver nanowires and TiO_2 were then prepared. The prepared silver nanowire/ TiO_2 composite paste and pure TiO_2 paste were coated onto ITO using a doctor blade method. After drying, the film was embossed. The working area was defined, and then high-temperature annealing was performed. The detailed steps for preparing the silver nanowire/ TiO_2 composite film are as follows.

1. Apply the silver nanowire/ TiO_2 composite paste and pure TiO_2 paste onto the ITO transparent conductive glass substrate using the doctor blade method, coating 3 to 5 times until the desired film thickness is achieved, then let it dry.
2. Emboss the coated samples with a pressure of approximately 20 kg/cm² for 60 s.
3. Define a working area of 0.25 cm² and use a glass slide to scrape off any excess film on the uniformly flat film.
4. Place the ITO transparent conductive glass substrate into a high-temperature furnace, add nitrogen gas, and perform heat treatment at 150°C for 90 min.
5. Increase the furnace temperature to 300°C for 30 min for annealing.

Next, the dye preparation and sensitization of the working electrode were carried out. In this experiment, N3 dye was used. The dye solution was prepared by mixing tert-butanol and acetonitrile in a specific ratio in a concentration of 3×10^{-4} M. N3 powder was then added to the mixed solution and sonicated for 2 h to ensure thorough dissolution and homogenization. The annealed silver nanowire and TiO_2 composite film were then soaked in the N3 dye solution and placed in an oven at 45°C for 2 h to enhance the sensitization speed of the electrode. This process allows the dye molecules to adhere uniformly to the film, improving its photoelectric conversion efficiency. After soaking, the film was rinsed with acetonitrile to remove any excess dye that did not bind to the surface. The glass outside the working area was then wiped with alcohol to ensure it was clean and free from any residual dye. Finally, the sensitized working electrode was dried thoroughly before encapsulation, ensuring that the dye molecules were firmly attached and the electrode was ready for the assembly of the solar cell. The electrolyte was prepared by combining 0.05 M I_2, 0.1 M LiI, and 1 M DMPII (1,2-dimethyl-3-propylimidazolium iodide). This mixture was then poured into 3-methoxypropionitrile and vigorously stirred using an ultrasonic homogenizer to prepare the electrolyte. In this study, platinum was chosen as the electrode material due to its excellent catalytic activity and corrosion resistance. The platinum film was deposited using an electron beam evaporation machine, where

platinum was evaporated at 10 mA for 45 s to obtain a thin film thickness ranging from one to several nanometers on the ITO glass conductive surface, completing the preparation of the electrode. In this study, we utilized the JEOL JSM-7500F field emission scanning electron microscope (FE-SEM) to observe a cold cathode. An X-ray Energy Dispersive Spectrometer (EDS) was also for the qualitative and quantitative analysis of micro-elements.

3. Results and Discussion

Silver nanowires were dispersed in an aqueous solution at a concentration of 20 mg/ml. The nanowires had an average diameter of approximately 90 nm and a length of about 60 μm. Silver nanowires possess exceptional electrical conductivity and optical properties, making them appropriate for applications such as transparent conductive films, sensors, and flexible electronic devices. The characteristics of the silver nanowires were provided by Uni-Onward Corp., which supplied the relevant physical property data and SEM image. The average diameter of the silver nanowires was 90 nm (Fig. 1). This fine structure significantly increases the surface area of the material, thereby enhancing its performance in conductivity and catalysis. The SEM image (Fig. 1) reveals the uniform distribution and consistent morphology of the silver nanowires, which are crucial for the reliability and reproducibility of experimental results.

Table 1. Specifications of silver nanowires.

Model	Diameter	Length	Purity	Transmission	Surface Resistivity
CG-001	90nm	60μm	99.5%	>96%	<20 ohm/sq

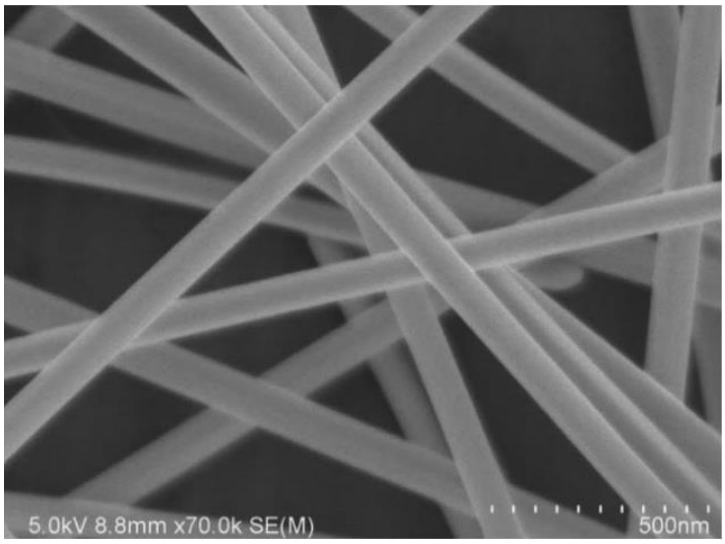

Figure 1. SEM image of the silver nanowires provided by Uni-Onward Corp.

We prepared composite slurries of TiO_2 and silver nanowires and applied them to ITO transparent conductive glass using a doctor blade method. FE-SEM was used to observe the surface morphology of the films, and tightly packed TiO_2 nanoparticles with numerous pores were observed. This porous structure facilitates the adsorption of more dye molecules on the working electrode surface, thereby enhancing the performance of DSSCs. Figure 2 illustrates the structure and morphology of the TiO_2/silver nanowires composite film. The composite structure formed by TiO_2 nanoparticles and silver nanowires increases the surface area and the light absorption of the electrode, improving photoelectric conversion efficiency. The presence of the porous structure allows for more efficient dye molecule adsorption in generating photocurrent.

TiO_2 and silver nanowire composite films were used in fabricating high-performance DSSCs in this study. TiO_2 nanoparticles, combined with silver nanowires increase surface area and light absorption and enhance photoelectric conversion efficiency. The porous films ensure the thorough adsorption of dye molecules, which is crucial for generating photocurrent. Moreover, the fabrication method of this composite material is simple and cost-effective for large-scale production, offering viable manufacturing of high-efficiency DSSCs. With optimization and adjustments, the performance of this composite material can be improved, which contributes to the advancement of solar cell technology. Single-point elemental analysis results using EDS revealed the composition of the doped elements in the film. The weights of Ti, O, and Ag were 50.94, 47.80, and 1.26 wt%. Ti and O were the predominant components of the film, with a minor presence of silver. The small percentage of silver suggests that it is a dopant, potentially enhancing the electrical properties of the film and improving efficiency of DSSCs.

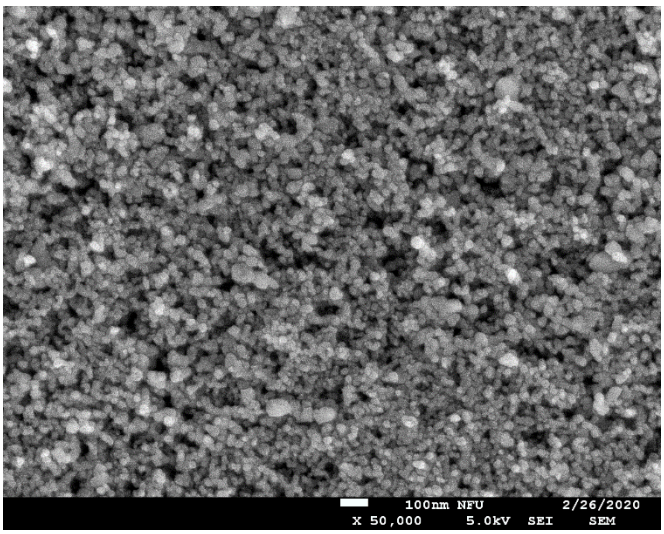

Figure 2. Top-view of the composite film fabricated in this study.

We explored the effect of the concentrations of silver nanowires on the performance of DSSCs. The concentrations were 0, 0.01, 0.03, 0.05, 0.07, 0.09, and 0.11 wt%. Table 1 presents the J-V characteristics for DSSCs with different silver nanowire concentrations. At a concentration of 0.05 wt%, the DSSCs achieved the highest open-circuit voltage (Voc), short-circuit current density (Jsc), and fill factor (FF), resulting in a peak efficiency of 4.14%. The efficiency was increased by 0.6% compared with (0 wt% without silver nanowires. The enhancement in performance at 0.05 wt% was attributed to the LSPR effect generated by the silver nanowires under light excitation. This effect led to the formation of a strong electromagnetic field, which enhances light absorption, charge separation, and the overall efficiency of the DSSCs. However, as the concentration of silver nanowires increased beyond 0.05 wt%, there was a noticeable decline in efficiency and other performance parameters. This decline was due to a reduction in dye loading on the TiO_2 photoanode, as excessive silver nanowires blocked the pores in the TiO_2 film. This blockage hampered the diffusion of the electrolyte into the TiO_2 film, limited the replenishment of electrons and ions at the photoanode/electrolyte interface, and thereby reduced the charge collection efficiency. While silver nanowires significantly enhanced the performance of DSSCs through plasmonic effects, an optimal concentration must be maintained to prevent detrimental effects. The results underscore the importance of optimizing the concentration of silver nanowires to balance enhanced light absorption with adequate dye loading and efficient charge transport. Future studies are needed to fine-tune the silver nanowire content and explore other metal nanostructures or combinations to enhance the performance of DSSCs. Additionally, the long-term stability and potential degradation mechanisms associated with the inclusion of silver nanowires are necessary for the application of the enhanced DSSCs.

Table 1. Characteristic parameters of silver nanowires at different concentrations.

Concentration	Voc (V)	Jsc (mA/cm^2)	Fill Factor (%)	Efficiency (%)
0wt%	0.70	7.71	65.20	3.54
0.01wt%	0.74	7.40	67.52	3.68
0.03wt%	0.73	7.54	69.12	3.82
0.05wt%	0.75	8.14	69.84	4.14
0.07wt%	0.74	7.97	67.49	4.07
0.09wt%	0.73	7.12	69.81	3.62

Figure 3 shows Nyquist plots of DSSCs with silver nanowires at different concentrations obtained using EIS. The series resistance R_s is influenced by the conductivity of the glass substrate, while the charge transfer resistance at the counter electrode/electrolyte interface R_{pt} is represented by the first semicircle in the high-frequency region. The resistance RkR_kRk, indicated by the second semicircle in the mid-frequency region, corresponds to the impedance at the photoelectrode/dye interface. The diffusion impedance within the electrolyte R_{DR}, shown by the third semicircle in the low-frequency region, represents the diffusion transport impedance. The resistance R_{kR} also indicates the recombination impedance of electrons and holes, where a higher resistance signifies more recombination. The effective rate constant of electron recombination K_{eff} is inversely related to the electron lifetime τ_{eff}; a higher K_{eff} indicates a faster recombination rate and shorter electron lifetime.

The analysis of these Nyquist plots reveals the electrochemical behavior of DSSCs with different concentrations of silver nanowires. At a concentration of 0.05 wt%, the devices exhibited the lowest impedance and the highest photoelectric conversion

efficiency, as depicted in Fig. 3. This optimal concentration facilitates efficient charge transport and minimizes recombination losses, leading to superior device performance. Conversely, at a concentration of 0.09 wt%, the increased concentration of silver nanowires adversely affected the conductivity between the counter electrode and the electrolyte, as evidenced by an increase in R_{pt}. This increase in resistance is attributed to the agglomeration of nanowires or saturation effects, which impede charge transport pathways. Additionally, the R_{DR} diffusion transport impedance increased, hindering the movement of ions within the electrolyte and exacerbating charge recombination. Consequently, the overall photoelectric conversion efficiency of the DSSCs decreased at a higher concentration. These findings underscore the importance of optimizing the concentration of silver nanowires in DSSC fabrication. While silver nanowires enhance conductivity and facilitate charge separation, excessive amounts lead to detrimental effects such as increased recombination and reduced efficiency. Additional research is required for fine-tuning the nanowire concentration and exploring alternative materials or configurations to achieve the best performance for DSSCs.

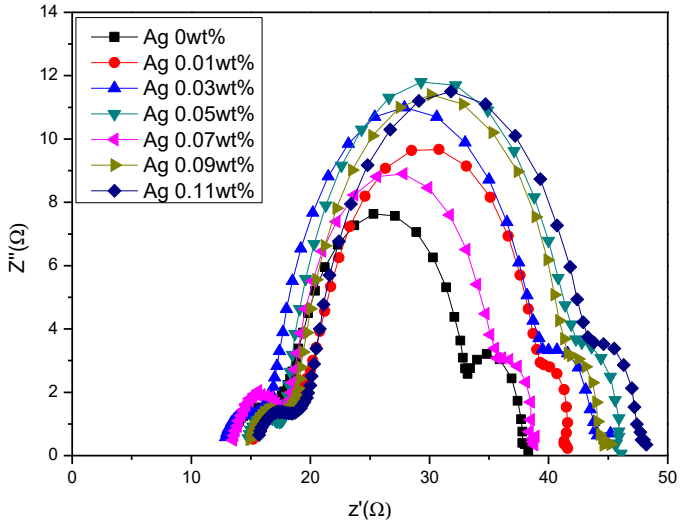

Figure 3. EIS analysis curves of silver nanowires at different concentrations.

Table 2 presents the IPCE analysis results at different concentrations. Efficiency was increased between the wavelengths of 450 and 550 nm. The efficiency reached its peak value in the range of 520 to 540 nm. Notably, the optimal photoelectric conversion efficiency was obtained at the concentration of silver nanowires of 0.05 wt%. At this concentration, the nanowires were effective in converting incident photons into electrical current, possibly due to optimal light absorption and scattering properties.

Table 2. IPCE characteristic parameters of silver nanowires at different concentrations

Concentration	Efficiency (%)	IPCE (%)	Wavelength(nm)
0 wt%	3.54	57.8	540
0.01 wt%	3.68	44.8	530
0.03 wt%	3.82	60.4	520
0.05 wt%	4.14	60.5	520
0.07 wt%	4.07	57.5	530
0.09 wt%	3.62	58.3	530
0.11 wt%	3.41	58.7	540

Table 3 shows the UV-Vis analysis results at different concentrations. This table presents the characteristic parameters obtained from UV-Vis measurements. UV-Vis analysis was used to assess the light absorption intensity of DSSCs. Measurements were conducted on the sensitized but not encapsulated working electrode of DSSCs. When 0.05 wt% silver nanowires were added to the working electrode, the dispersion effect became optimal. This resulted in the uniform dispersion of TiO_2 and an increased amount of dye adsorption. Given that the absorption peak of N3 dye was found at around 538 nm, all concentrations declined in light absorption beyond 538 nm due to insufficient light absorption.

Table 3. UV-Vis characteristic parameters of silver nanowires at different concentrations.

Concentration	Efficiency (%)	Absorbance	Wavelength (Nm)
0 wt%	3.54	2.823	448

0.01 wt%	3.68	2.892	409
0.03 wt%	3.82	2.805	422
0.05 wt%	4.14	3.190	460
0.07 wt%	4.07	2.609	437
0.09 wt%	3.62	2.457	415
0.11 wt%	3.41	2.674	482

4. Conclusions

We investigated the effect of adding silver nanowires of different concentrations on the working electrode of DSSCs. Silver nanowires at a concentration of 2 mg/ml were mixed into TiO_2 paste and applied to ITO-coated glass substrates using a blade-coating method. To ensure accuracy, the film thickness was maintained at approximately 10 μm. The solar cells were then assembled using a sandwich method, which involved heating and sealing the photoanode, thermoplastic film, and counter electrode. J-V curves and IPCE data revealed that a 0.05 wt% concentration of silver nanowires achieved the highest photovoltaic conversion efficiency of 4.14%, with an open-circuit voltage of 0.75 V and a current density of 8.14 mA/cm². This represented an increase of 16.9% in efficiency compared with that of DSSCs without silver nanowires. The cells demonstrated the best electron lifetime and the lowest electron-hole recombination rate. EIS measurement results indicated that the solver nanowire concentration of 0.05 wt% resulted in the lowest Rs, Rpt, Rk, and Keff. This suggests that an optimal amount of silver nanowires effectively enhances photovoltaic efficiency by reducing electron-hole recombination and providing a high specific surface area to increase light absorption. The silver nanowire concentration of 0.05 wt% allowed for the highest efficiency due to the strong electromagnetic fields generated by LSPR when excited by light. This increased the photogenerated electron density and improved the short-circuit current density and overall efficiency of the DSSCs.

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