

The Characterization of Dye-sensitized Solar Cell with Photoelectrode Modified by TiO₂/GO/Ag Nanofibers at Low Light Intensity

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ABSTRACT

Titanium dioxide (TiO₂) nanofibers (NF) including graphene oxide (GO) and silver (Ag) nanoparticles (NPs) were prepared using the sol-gel method and electrospin technique. The photovoltaic conversion efficiency (η) of the modified dye-sensitized solar cell (DSSC) with TiO₂/GO/Ag nanofibers on the photoelectrode was measured under various low light intensities. The incorporation of GO and Ag nanoparticles led to rapid electron transport and a reduced incidence of electron recombination. The synthesized TiO₂/GO/Ag nanofibers had a large specific surface area and high porosity that promoted dye absorption at the photoanode. The η of the TGAP modified photoelectrode was 34% higher than that of a standard DSSC photoelectrode. This study showed that the highest η for the TGAP modified photoelectrode was 6.56% which occurred at 30 mW/cm², this was attributed to the decreased electron recombination under those low light conditions.

Keywords: Dye-sensitized Solar Cell (DSSC), Electrospinning, Nanofiber, Low Illumination.

1. INTRODUCTION

In 1991, Swiss scientists O'Regan and Michael Grätzel were the first to develop a dye-sensitized solar cell which they covered in their manuscript "A low cost, high-efficiency solar cell based on dye sensitized colloidal TiO₂ film" (O'Regan and Grätzel, 1991), published in the journal Nature. In recent years, more scientists have investigated dye-sensitized solar cells (DSSCs), because they are a cost-effective photovoltaic device, with key

specific advantages such as the simple manufacturing process, low cost, lower time consuming, and greater flexibility in different environments such as lower illumination (O'Regan and Grätzel 2011; Yella *et al.* 2011; Qiu *et al.* 2011; Balasingam *et al.* 2013a; Balasingam *et al.* 2013b). Hence, DSSC are a highly promising photovoltaic device. DSSCs are composed of a photoelectrode, an electrolyte and a counter electrode. In general, the material used for the photoelectrode is titanium dioxide (TiO₂), because TiO₂ is compatible with dye molecules. The photoelectrode of DSSC plays a very important role as it takes responsibility for transforming the available light into electric power (Obotowo *et al.* 2016). Different researchers have experimentd with different materials to improve the performance of DSSCs photoanodes, with good results. Motlak *et al.* modified a photoanode with N-doped TiO₂ nanofibers, and the photoelectric conversion efficiency reached 4.7% (Motlak *et al.* 2014). Mahmoud *et al.* modified a photoanode with S-doped TiO₂ nanofibers, and the photoelectric conversion efficiency reached 4.27% (Mahmoud *et al.* 2018). Kouhestanian *et al.* doped a TiO₂ photoanode with ZnO, and the photoelectric conversion efficiency reached 5.12% (Kouhestanian *et al.*, 2020). The relatively high conversion efficiency of DSSCs under low illumination is also subject to investigation; for instance N. M. Mohamed *et al.* (Mohamed *et al.* 2015) showed that DSSCs performed better under diffused light conditions, thus they were better suited to cloudy environments and vertical installation in integrated photovoltaic systems for buildings. In addition, Marina Freitag *et al.* (Freitag *et al.* 2017) showed that DSSCs were ideally suited to ambient light environments because they are able to harvest that energy to power electronic devices or to extend their battery lifetime. In a previous study, these authors developed the modified DSSC structure shown in Fig. 1, and the test results under low illumination were presented in (Nien *et al.* 2020).

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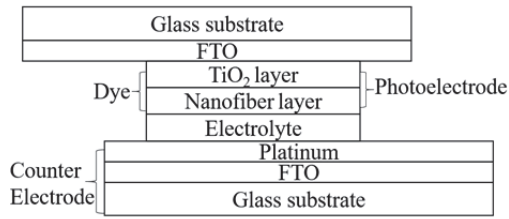


Fig. 1 Schematic diagram of the DSSC in this study

2. MATERIALS AND METHODS

The chemicals used in this study are as follows: titanium (IV) isopropoxide (TTIP), polyvinylpyrrolidone (PVP, $M_w = 1,300,000$), acetic acid (CH_3COOH), silver nitrate (AgNO_3), and alcohol ($\text{CH}_3\text{CH}_2\text{OH}$, Choneye Pure Chemical, Taiwan). Phthalocyanine was purchased from Aldrich, in the USA. The titanium dioxide (TiO_2) powder (P25) and Ruthenium-535 (N3) were obtained from UniRegion Bio-Tech, Taiwan. The iodine puriss (I_2) was obtained from Riedel-de Haën, Germany.

The acetic acid and alcohol were used as solvents. The TiO_2 nanofibers (NF) composited with graphene oxide (GO) and Ag nanoparticles (NPs) were manufactured by electrospinning. The photoelectrode was prepared by doctor blade method, where the TiO_2 was pasted onto the fluorine-doped tin oxide (FTO) glass. Then the $\text{TiO}_2/\text{GO}/\text{Ag}$ NF was seeded on the TiO_2 paste as an additional layer on the DSSC photoelectrode (Nien *et al.* 2019)

The photoelectrode was heated at 450°C for 30 minutes then soaked in N3 dye for 24 hours. The counter electrode was platinum and fabricated by radio frequency (R. F.) sputtering the platinum onto the FTO glass substrate. An iodide electrolyte was then introduced between the electrodes. The $\text{TiO}_2/\text{GO}/\text{Ag}$ NF modified photoelectrode, referred to as TGAP, was completed. For comparison and reference purposes, the pure TiO_2 photoelectrode was also fabricated by doctor blade method and is referred to as TiO_2 .

In order to compare the relative photovoltaic performances of TGAP and TiO_2 under different illumination levels, the photovoltaic parameters of the two DSSCs were measured under a variety of illumination levels. The light intensity was adjusted using a solar simulator (MFS-PV-Basic-HMT, Taiwan) where the measured light intensities were $100 \text{ mW}/\text{cm}^2$, $80 \text{ mW}/\text{cm}^2$, $50 \text{ mW}/\text{cm}^2$, $30 \text{ mW}/\text{cm}^2$ and $10 \text{ mW}/\text{cm}^2$, respectively. The resistance across the interface between the photoelectrode and electrolyte was measured by electrical impedance spectroscopy (EIS, BioLogic SP-150, France), with a scanning frequency between 1 and 50 MHz.

3. RESULTS AND DISCUSSION

Table 1 and Table 2 are the photovoltaic parameters under different light intensities for the two DSSCs with either the TiO_2 or TGAP photoelectrode, respectively. It can be seen from Table 1 and Table 2 that the photovoltaic conversion efficiencies (η) of the two DSSCs photoelectrodes at $100 \text{ mW}/\text{cm}^2$ were 4.03 % for the TiO_2 , and 5.40 % for the TGAP. The photoelectric conversion efficiency of the photoanode modified by $\text{TiO}_2/\text{GO}/\text{Ag}$ nanofibers increased by 34% which was an excellent conversion efficiency. The main reason for increase in efficiency can be attributed to the $\text{TiO}_2/\text{GO}/\text{Ag}$ nanofibers increasing dye absorption which promotes electron transfer (Nien *et al.* 2019). The corresponding current density–voltage (J-V) curves for the two different photoelectrodes are shown in Fig. 2 and Fig. 3, respectively. According to Fig. 3 and Table 2, the photovoltaic conversion efficiency (η) of DSSCs using TGAP increases from 5.40% to 6.56% under lower light intensity, from $100 \text{ mW}/\text{cm}^2$ to $30 \text{ mW}/\text{cm}^2$. In addition, Table 1 shows the η of the TiO_2 based DSSCs increasing from 4.03% to 4.90% during a decrease in light intensity from $100 \text{ mW}/\text{cm}^2$ to $30 \text{ mW}/\text{cm}^2$. From Table 1 and Table 2, it can be seen that both J_{sc} and V_{oc} decrease, and output power decreases, as light intensity decreases from $100 \text{ mW}/\text{cm}^2$ to $10 \text{ mW}/\text{cm}^2$. In other words, it is possible to improve the utilization of optical power under low illumination. The amount of photons decreases as light intensity decreases, which causes a decrease in excitement of the dye molecules, leading to a reduction in J_{sc} . The lower J_{sc} can be attributed to the decrease of photogenerated electrons (Zhai *et al.* 2016). Because of the decreased light intensity, the electrons in the conductive band are reduced, which reduces the quasi Fermi level of the TiO_2 . The gap between the quasi Fermi level of the TiO_2 and the redox potential of the electrolyte is reduced, resulting in a decrease in V_{oc} . This means that DSSCs can decrease recombination reactions to enhance η under low illumination conditions. The decrease in light intensity reduces the quasi-Fermi energy level of the TiO_2 and reduces the gap with the oxidation-reduction potential, finally reducing the V_{oc} . Due to the low energy band gap of Ag, in theory the V_{oc} of the TGAP photoanode should be less than that of the TiO_2 photoanode. However, because of the good conductivity of Ag, electrons are quickly transferred and electron recombination is reduced. In addition, the photoanode modified with nanofibers has better photovoltaic performance due to the Surface Plasmon Resonance (SPR) phenomenon, which increases the photon collection ability (Pal *et al.* 2017). The fill factor increases as the light intensity reduces. For the two different photoelectrodes, the highest η are all observed at an intensity of $30 \text{ mW}/\text{cm}^2$. When the photoelectrode is TGAP, the maximum η of 6.56 % is achieved. When attributable light intensity is too low, for example at $10 \text{ mW}/\text{cm}^2$, η decreases.

Table 1 TiO_2 Based DSSC parameters.

Intensity (mW/cm^2)	R_s (Ω)	R_1 (Ω)	R_2 (Ω)	J_{sc} (mA/cm^2)	V_{oc} (V)	F. F. (%)	η (%)
100	20.59	7.96	37.28	8.24 ± 0.11	0.71 ± 0.03	68.97 ± 0.16	4.03 ± 0.12
80	21.03	8.53	40.90	6.96 ± 0.13	0.70 ± 0.02	70.10 ± 0.14	4.27 ± 0.13
50	21.61	9.09	59.95	4.71 ± 0.12	0.69 ± 0.04	71.16 ± 0.16	4.62 ± 0.11
30	23.65	9.81	83.38	3.04 ± 0.11	0.67 ± 0.05	72.08 ± 0.15	4.90 ± 0.12
10	24.31	13.51	220.91	0.93 ± 0.14	0.66 ± 0.03	70.53 ± 0.13	4.24 ± 0.14

Table 2 TGAP based DSSC parameters.

Intensity (mW/cm ²)	R _s (Ω)	R ₁ (Ω)	R ₂ (Ω)	J _{sc} (mA/cm ²)	V _{oc} (V)	F. F. (%)	η (%)
100	18.09	9.72	42.83	10.13 ± 0.13	0.76 ± 0.06	70.15 ± 0.12	5.40 ± 0.12
80	18.60	10.76	51.89	8.36 ± 0.16	0.75 ± 0.03	70.97 ± 0.13	5.56 ± 0.13
50	19.36	11.51	75.93	5.66 ± 0.12	0.74 ± 0.04	72.18 ± 0.15	6.01 ± 0.15
30	22.01	13.52	105.56	3.75 ± 0.12	0.72 ± 0.03	72.95 ± 0.13	6.56 ± 0.14
10	22.80	17.95	279.08	1.12 ± 0.13	0.70 ± 0.05	71.02 ± 0.12	5.59 ± 0.11

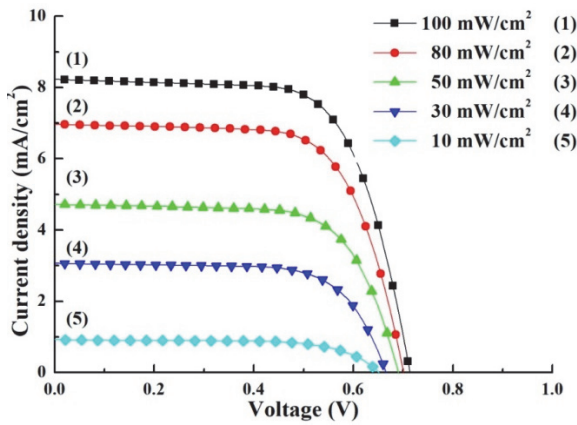


Fig. 2 Current density–voltage curves of the TiO₂ based DSSC under different illuminations.

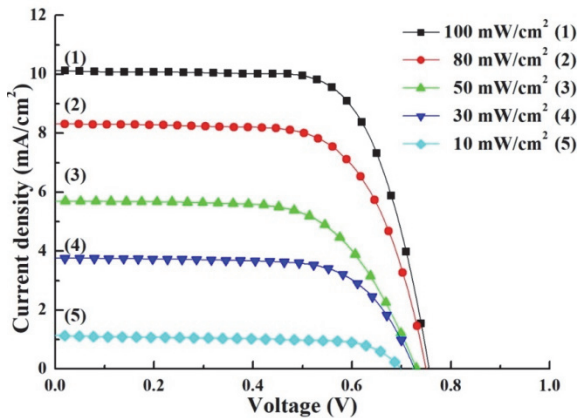


Fig. 3 Current density–voltage curves of the TGAP based DSSC under different illuminations.

According to Fig. 4 and Fig. 5, which are the Nyquist plots of the two DSSCs based on TiO₂ and TGAP under different illuminations, it can be seen that impedance becomes much larger with a decrease in light intensity. These impedances from the Nyquist plots indicate that there is a lower probability of reverse recombination (dark reaction). The amount of photo-generated electrons reduces with the decrease in light intensity. Moreover, it contributes an improvement to the fill factor (F.F.). This is the reason why the DSSC can improve photovoltaic conversion efficiency. Table 2 shows that R_s lies between 18.09 Ω and 22.80 Ω. R₁ increases from 9.72 Ω to 17.95 Ω, and R₂ increases from 42.83 Ω to 279.08 Ω. Moreover, the lower photovoltaic conversion efficiency under the lowest possible illumination is due to there being fewer photo-generated electrons. The larger impedance indicates less photo-generated electrons are at the interface of the TiO₂/electrolyte and the electrolyte/counter electrode.

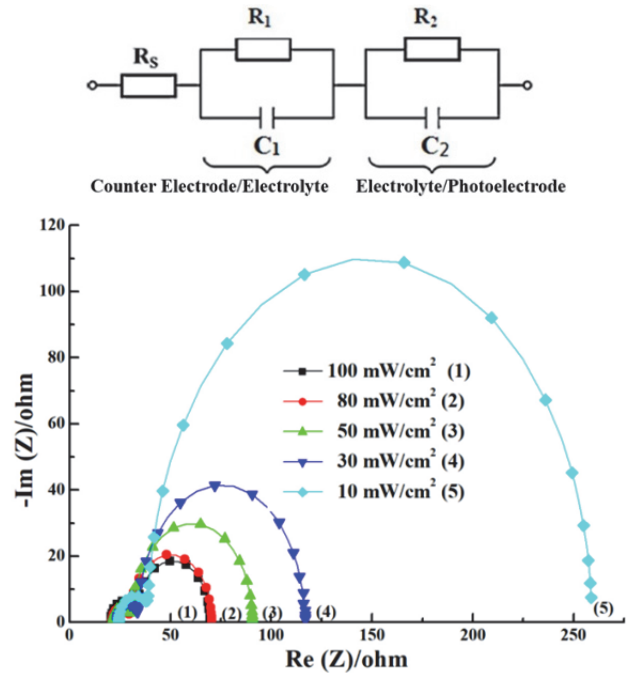


Fig. 4 Nyquist plots for TiO₂ based DSSCs under different illuminations.

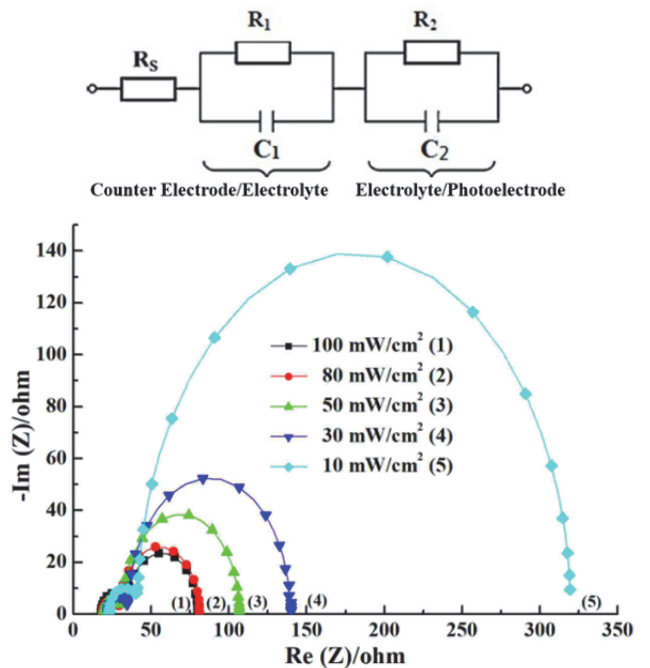


Fig. 5 Nyquist plots for TGAP based DSSCs under different illuminations.

4. CONCLUSION

In summary, the dye-sensitized solar cell modified with TiO₂/GO/Ag NF as an additional layer on the photoelectrode shows a photovoltaic conversion efficiency (η) increase from 5.40% to 6.56% under light intensities that decrease from 100 mW/cm² to 30 mW/cm². The DSSCs decrease the recombination of electrons to enhance η under low illumination conditions. This phenomenon shows that further optimization of DSSCs for use in low light conditions is possible with continued investigation.

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