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Photovoltaic Performance Analysis of Dye-Sensitized Solar Cell With ZnO Compact Layer and TiO₂/Graphene Oxide Composite Photoanode

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ABSTRACT In this paper, the photoanode of dye-sensitized solar cell (DSSC) was fabricated as a double layer structure, where graphene oxide (GO) was incorporated with titanium dioxide (TiO₂) film onto the ZnO compact layer. The photovoltaic characteristics, crystal structures, morphologies, and electrochemical impedance were investigated. According to the experimental results, the photovoltaic performance of DSSC was improved with the modification of ZnO compact layer and GO. The phenomenon can be attributed to the higher specific surface area of GO and the property of forming an energy barrier between the substrate and TiO₂ film for ZnO compact layer, which can inhibit the electron-hole recombination.

INDEX TERMS Dye-sensitized solar cell, graphene oxide, titanium dioxide, ZnO, compact layer, photovoltaic characteristics.

I. INTRODUCTION

In recent years, there is a growing number of researches regarding renewable energy resources. Among them, solar energy is particularly suitable to develop because its inexhaustibility in supply and non-poisonous material for environment. Dye-sensitized solar cell (DSSC) got a lot of attentions since Swiss scientist Michael Grätzel reported the DSSC with a conversion efficiency (η) over 7%, which contained nano-porous TiO₂ in 1991 [1]. In terms of photovoltaic efficiency, in order to achieve the maximum dye-loading, the deposition of TiO₂ nanoparticles on a conducting oxide-coated glass has been widely studied [2], [3].

For the DSSC, recombination of electron-hole pairs will decrease the photovoltaic performance. One method to avoid the photovoltaic performance decrease is using the compact layer, which is usually fabricated between the transparent conducting oxide (TCO) and the semiconductor to prevent the back electron transfer occurring in the interface

between electrolyte and TCO. Besides, a suitable thickness of compact layer will increase the open-circuit voltage (V_{oc}), which leads to the efficiency enhancement of DSSC. Several metal oxide materials have been explored for the compact layer, such as TiO₂ [4], Nb₂O₅ [5], In₂O₃ [6], ZnO [7], MgO [8] and NiO [9]. Among these materials, TiO₂ compact layer receives much discussion because TiO₂ compact layer can effectively improve adherence of TiO₂ to fluorine doped tin oxide (FTO) surface, which provided a larger TiO₂/FTO contact area and reduced the electron recombination by separating the direct contact between conductive FTO surface and the redox electrolyte [10], [11]. Unfortunately, TiO₂ compact layer can not improve the V_{oc} because it has the same conduction band energy of TiO₂ adsorption layer. Thus, it is necessary to fabricate the compact layer by choosing another material.

ZnO nanostructures have multifunctional properties with high exciton binding energy, low resistivity, non-toxicity,

high transparency in the visible range, high light trapping characteristics, and excellent electron transport characteristics to reduce the recombination between electron and hole [12]–[14]. It was reported that the ZnO compact layer can form an energy barrier between TiO₂ and FTO substrate. Because ZnO has the more negative conduction band edge than that of TiO₂, it will restrain the recombination reaction and improve V_{oc} at the same time [7].

It is well known that graphene oxide (GO) is a potential nanomaterial for DSSC, which has a large specific surface area (2630 m²/g). Thus, it can enhance the dye-loading and increase the photogenerated electrons [15]. GO also has high activity to assist the catalytic process. Besides, Xu *et al.* [16] demonstrated that GO multilayer films could be used as an efficient counter electrode, and the conversion efficiency was improved. Gao *et al.* [17], [18] developed GO to modify the anode interface of inverted bulk-heterojunction (BHJ) polymer solar cells. Besides, the device with GO demonstrated a remarkable improvement in conversion efficiency, indicating that GO can effectively modify the BHJ/metal anode interface to facilitate efficient hole collection.

In this study, we reported a special double layer structure for photoanode of DSSC. The first layer of photoanode was ZnO compact layer and the second layer was TiO₂/GO layer. Photovoltaic performances of ZnO compact layer and TiO₂/GO layer for DSSC were investigated. The experimental results demonstrated that the photovoltaic performance was improved when the DSSC was modified by this double layer structure. Finally, the achieved η is 3.19%, showing that the DSSC with a double layer photoanode had the potential to develop into the photovoltaic charger.

II. EXPERIMENTAL

A. MATERIALS

ZnO target was purchased from Ultimate Materials Technology Co., Ltd., Taiwan. TiO₂ powder and Ruthenium-535 (N3) were purchased from UniRegion Bio-Tech, Taiwan. Graphite powder was purchased from Energe Inc., Taiwan. The Triton X-100 was purchased from PRS Panreac, Spain. The acetylacetone (AcAc), lithium iodide (LiI) and 4-Tert-Butylpyridine (TBP) were purchased from Sigma-Aldrich, United States. The ethanol was purchased from Katayama Chemical, Japan. The 1-propyl-2,3-dimethylimidazolium iodide (DMPII) was purchased from Tokyo Chemical, Japan. The iodine (I₂) was purchased from Riedel-deHaen, United States.

B. SYNTHESIS OF THE GRAPHENE OXIDE

The GO powders were synthesized from graphite powders via the modified Hummer's technology. First of all, we added KMnO₄ gradually to the mixed solution after putting the graphite/sodium nitrate (NaNO₃) and sulfuric acid (H₂SO₄) in a sealed container. Then, the mixed solution was allowed to stand for 1 hour in an ice-water bath, and stirred for 48 hours. After that, deionized (D. I.) water was added to the mixed solution and H₂O₂ was added to stir and

stood for 24 hours. Afterwards, we used a mixed solution of hydrochloric acid (HCl)/H₂O (vol. ratio: 1/10) to wash the obtained product. Further, the precipitation was washed by D. I. water to the 7.0 pH and then freeze-dried to remove water for the purpose of obtaining GO powders. Finally, the GO powders was added to D. I. water (vol. ratio: 100 mg/100 mL) to form a mixed solution. The synthesis diagram of GO was shown in Fig. 1.

C. FABRICATION OF THE DYE-SENSITIZED SOLAR CELL

The photoanode is a double layer structure, which includes ZnO compact layer and TiO₂/GO layer. A ZnO target with a purity of 99.99 % was sputtered in a reactive gas mixture of Ar and O₂ with a pressure ratio Ar/O₂ of 9/1. The pressure of the sputtering chamber was set to 3 mTorr and the R.F. power was set to 60 W to fabricate the ZnO compact layer on the FTO glass. Moreover, we dropped the TiO₂/GO colloid on the ZnO compact layer by spin-coating method. The TiO₂/GO colloid was composed of 3 g TiO₂ powders, 4 mL D. I. water, 0.05 mL AcAc, 0.15 mL Triton X-100 and 2 mL GO. Next, the active area of DSSC was set to 0.64 cm² and the photoanode was immersed in 3×10^{-4} M N3 dye solution for 24 hours after annealing at 450°C for 30 minutes. The liquid electrolyte consisted of 0.6 M 1-propyl-2,3-dimethylimidazolium iodide (DMPII), 0.5 M lithium iodide (LiI), 0.05 M iodine (I₂), and 0.5 M 4-tert-butylpyridine (TBP) in 15 mL 3-methoxypropionitrile (MPN). Furthermore, the platinum (Pt) counter electrode of DSSC was fabricated by sputtering in a 10 sccm reactive gas of Ar, where the pressure of the sputtering chamber was set to 30 mTorr and the R.F. power was set to 60 W. Finally, the photoanode, electrolyte and Pt counter electrode were assembled into a sandwich cell structure, which was shown in Fig. 2.

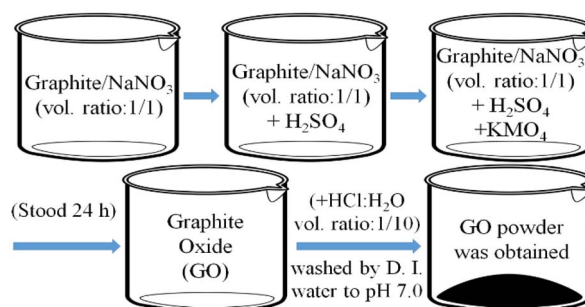


FIGURE 1. The synthesis diagram of graphene oxide.

D. MEASUREMENT SYSTEM AND PHOTOELECTRIC CHARACTERISTICS OF THE PHOTOANODES

The morphologies of photoanodes were observed by scanning electron microscope (SEM) (JEOL 5410LV, Japan). The crystal structures of photoanodes were determined by X-ray diffraction (XRD) using a Rigaku D/MAX2500

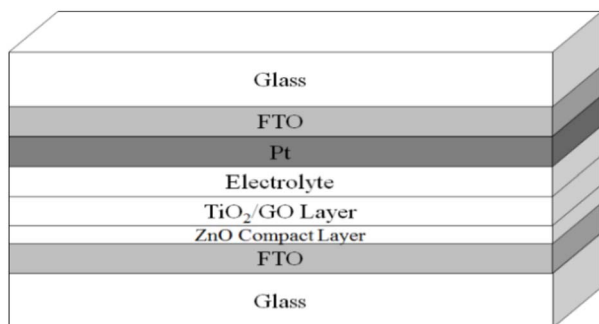


FIGURE 2. The structure of the DSSC including ZnO compact layer and TiO₂/GO layer.

diffractometer with Cu K α ($\lambda = 1.5406 \text{ \AA}$) radiation operated at 40 kV and 100 mA via a scan rate of $2^\circ/\text{min}$. The photovoltaic characteristics of DSSC were measured by a solar light simulator (MFS-PV-Basic-HMT, Taiwan), which was employed to simulate sunlight under one sun AM 1.5 G (100 mW/cm^2) illumination provided by a 1000 W Xenon (Xe) lamp. The α -step surface profilometer was utilized to measure the thickness. Through LVDT (Linear Variable Differential Transformer), an electronic analog signal is produced and converted to digital signals and the signals were transmitted to a computer control system in order to generate a signal chat. The electrochemical impedance spectroscopy (EIS) measurements of photoanodes were performed by an electrochemical analyzer (BioLogic SP-150, France) with frequency range from 1 MHz to 50 mHz using an AC perturbation signal of 10 mV.

III. RESULTS AND DISCUSSION

A. CHARACTERIZATIONS OF THE PHOTOANODES WITH DIFFERENT STRUCTURES

The surface condition of top-view SEM micrographs for different photoanode structures were shown in Fig. 3. In Fig. 3(a), the ZnO compact layer was observed. ZnO compact layer can reduce the back electron transfer occurring in the interface between electrolyte and TCO [19]. Figure 3(b) showed the TiO₂ thin film which dispersed on the ZnO compact layer uniformly. It can be found that TiO₂ particles combined with each other after annealing at 450°C for 30 minutes. Figure 3(c) showed the curled GO sheets with an accelerating voltage of 50 kV. Moreover, TiO₂/GO fabricated on the top of ZnO thin film was exhibited in Fig. 3(d). Owing to the evaporation of H₂O, the functional groups and acidic residues in TiO₂/GO fabricated on the top of ZnO composite film were oxidized after annealing process, which extended the porosity of film and enhanced light scattering [20], [21]. In addition, the porosity can enhance the dye-loading and increase the photo-generated electrons.

Figure 4 showed the XRD patterns with the detection range from 20° to 80° of ZnO, TiO₂, GO and the composite

materials, which were employed in the photoanodes of DSSC. The different films and structures were confirmed according to the Joint Committee on Powder Diffraction Stands Card File No. 21-1272 (standard diffraction data of anatase TiO₂) and 76-1940 (standard diffraction data of rutile TiO₂) [22], [23]. It could be seen that the diffraction peak of composite film, when GO was incorporated into the photoanode of DSSC, appeared at $2\theta = 30^\circ$, $2\theta = 36^\circ$, $2\theta = 50^\circ$ and $2\theta = 62^\circ$. The phenomenon could be attributed to that GO substituted Ti's position and thus the crystallization of TiO₂ was changed [24]. Besides, the content of GO was greatly fewer than TiO₂ in TiO₂/GO colloid. Moreover, the diffraction peak of TiO₂ and GO composite material nearby $2\theta = 12^\circ$ was difficult to be observed in reference [25]. The phenomenon can be attributed to TiO₂ coated with GO uniformly. Thus, we considered that the two reasons cause the diffraction peak of TiO₂ and GO composite material nearby $2\theta = 12^\circ$ was difficult to be observed. Additionally, the grain size D of TiO₂ and TiO₂/GO fabricated on the top of ZnO photoanode were estimated by the Debye-Scherrer formula (1) [26].

$$D = \frac{0.9\lambda}{\beta \times \cos\theta} \quad (1)$$

where D is the grain size of the TiO₂ film, λ is the wavelength of X-Ray (0.154 nm), β is the full width at half maximum, and θ is the diffraction angle [27]. The XRD data of TiO₂ and TiO₂/GO fabricated on the top of ZnO photoanodes were shown in Table 1.

TABLE 1. The XRD data of TiO₂ and ZnO+TiO₂/GO composite films.

photoanode	2θ ($^\circ$)	$\sin\theta$	$\cos\theta$	β (10^{-3})	D (nm)
TiO ₂	25.26	0.22	0.98	9.51	14.87
ZnO+TiO ₂ /GO	25.26	0.22	0.98	8.90	15.88

B. PHOTOVOLTAIC CHARACTERISTICS OF DIFFERENT PHOTOANODE STRUCTURES

In Fig. 5, J-V curves of DSSC with different photoanodes were shown, and the photovoltaic parameters were listed in Table 2. It can be seen that the η of DSSC with ZnO compact layer (ZnO+TiO₂ layer) are higher than that of the pure TiO₂DSSC. The phenomenon can be attributed to the excellent characteristics of ZnO compact layer, which formed an energy barrier between FTO substrate and TiO₂ film to inhibit electron injection from the conduction band of TiO₂ to FTO. While for the photoanode with TiO₂/GO fabricated on the top of ZnO, GO has a high specific surface area, which could increase the dye loading from photoanode and enhance the conduction path for electron in the internal structure of DSSC [28]–[30]. Furthermore, GO acted as a bridge to improve the electron transport in DSSC [31]. Besides, the thickness is also a key point to affect the dye

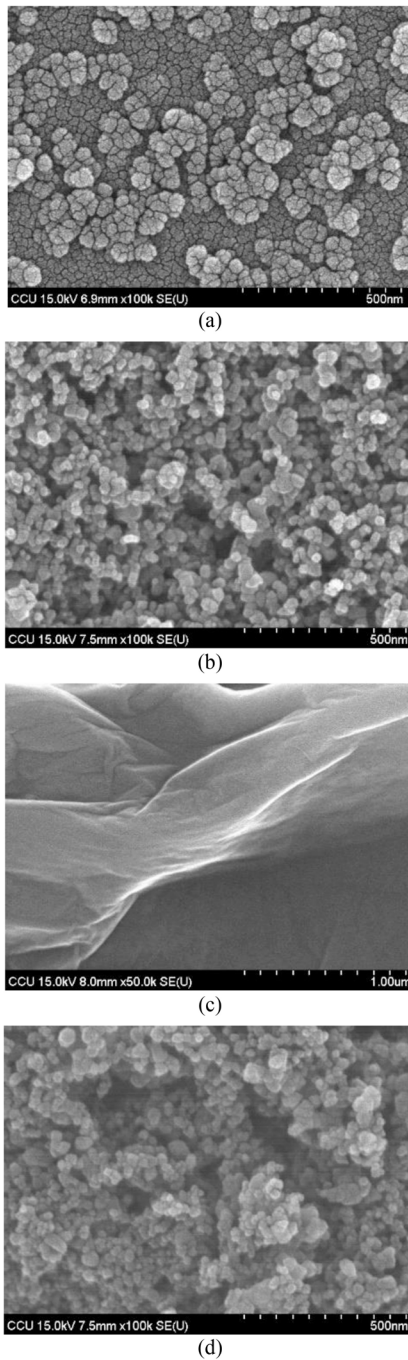


FIGURE 3. The top-view SEM micrographs of (a) ZnO compact thin film, (b) ZnO+TiO₂ thin film, (c) GO thin film and (d) ZnO+TiO₂/GO thin film.

loading, which can influence the amount of photogenerated electrons [32], [33]. The structure of TiO₂/GO fabricated on the top of ZnO has the thickest thickness (11.17 μm) than other structures. Thus, it made the highest short-circuit current density (J_{sc}) achieved 7.19 mA/cm². In the meanwhile, η achieved 3.19 %. However, the V_{oc} was slightly lower because the condition of recombination reaction was enhanced. It can be attributed to the increasing concentration of I_3^- .

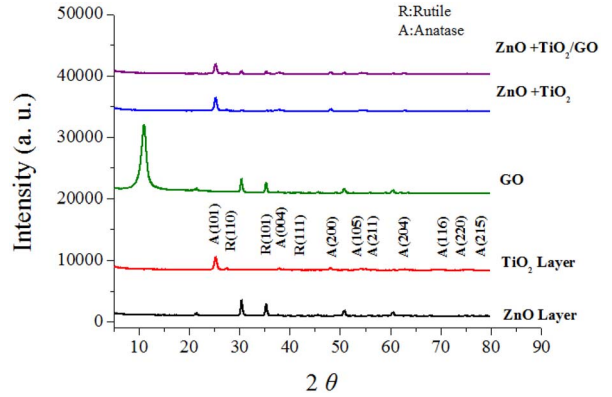


FIGURE 4. The XRD patterns of different films.

It is observed that the DSSC with pure ZnO compact layer for the photoanode has a poor η . The surface condition of ZnO nanostructure is an important factor in determining the performance of DSSC because dissolved Zn^{2+} and dye on the ZnO surface lead to aggregation, which decreases injection efficiency. Thus, the worse interaction between dye and ZnO reduces the light harvesting efficiency [34]. The aggregates remained in the mesoporous structure, which provided the absorption of light, but no electron injection occurred, and thus strongly affected the performance of DSSC. It is the reason why pure ZnO nanostructure can not be used as the photoanode directly.

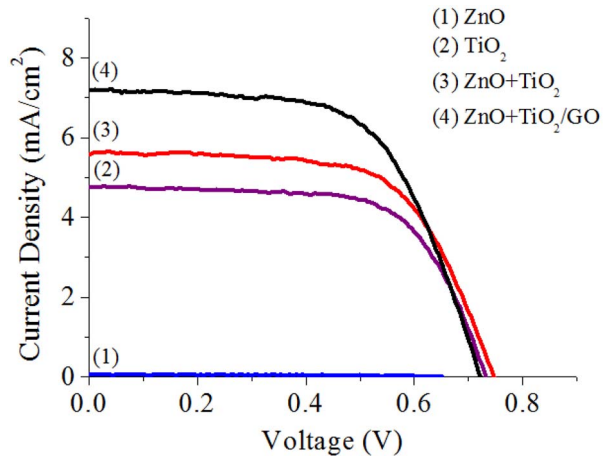


FIGURE 5. The J-V curves of DSSC with different photoanodes.

C. EIS MEASUREMENTS OF DIFFERENT PHOTOANODE STRUCTURES

In DSSC device, the charge was collected at the interface by solid/solid or solid/liquid reaction, the electrochemical reaction of charge, ion and electron were produced, the characteristics of above reactions which could be interpreted as capacitance, resistance and inductance. The Nyquist plots was simulated by EIS with an equivalent circuit model, which was formed by a real value (Z') and imaginary value (Z''), where the real axis is called resistance and the

TABLE 2. The photovoltaic parameters of DSSC with different photoanodes.

Photoanode	Thickness (μm)	V_{oc} (V)	J_{sc} (mA)	F.F. (%)	η (%)
ZnO	0.03	0.65	0.06	58.82	0.02
TiO ₂	10.02	0.73	4.75	66.63	2.31
ZnO+TiO ₂	10.25	0.74	5.58	64.74	2.69
ZnO+TiO ₂ /GO	11.17	0.72	7.19	61.51	3.19
TiO ₂ [35] (2014)	10.60	0.77	7.20	53.40	2.96
ZnO [36] (2014)	9.00	0.40	3.15	34.00	0.43
TiO ₂ /GO [37] (2012)	N/A	0.67	7.60	54.00	2.78

imaginary axis is called capacitive reactance, as shown in Fig. 6. Besides, the equivalent circuit model of DSSC in this study was exhibited in Fig. 7.

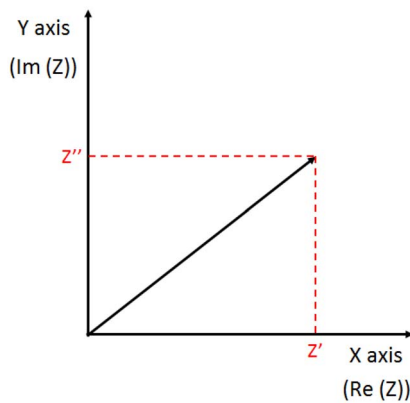


FIGURE 6. The scheme of Nyquist plot.

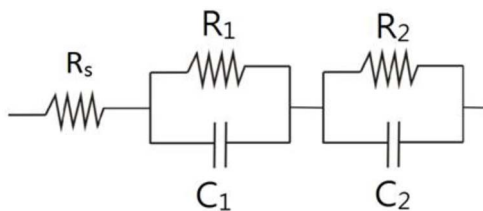


FIGURE 7. The equivalent circuit model of dye-sensitized solar cell.

Figure 8 (a) and (b) showed the Nyquist plots, which can explain the changes of internal impedance for the DSSC with different photoanode structures. The X-axis intercept in Nyquist plots represents the serial resistance between

wire of measurement and FTO glass (R_s). Besides, the first semicircle in the impedance spectra at high frequency represents the impedance between platinum (Pt) counter electrode and electrolyte (R_1). Moreover, the second semicircle in the impedance spectra at intermediate frequency represents the impedance between electrolyte and TiO₂ film (R_2) [38]. Table 3 showed the performances of EIS with different photoanodes. It can be seen that R_2 decreases from 50.42 Ω to 7.26 Ω when photoanode structure of TiO₂/GO fabricated on the top of ZnO, which can restrain the recombination of electron-hole and the dark reaction at R_2 [39]. Thus, the electron transfer was improved and the η was enhanced. In addition, high specific surface area of GO has the ability to provide a charge transmission and to reduce the dark reaction of DSSC.

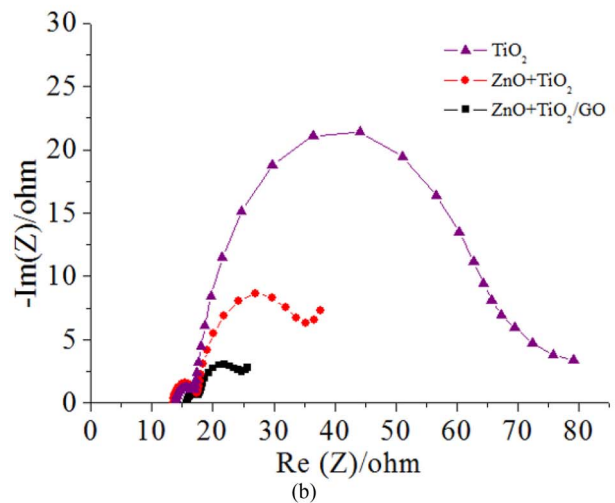
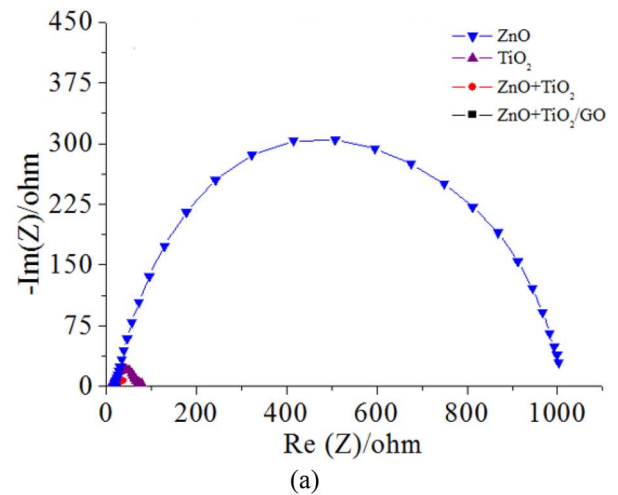
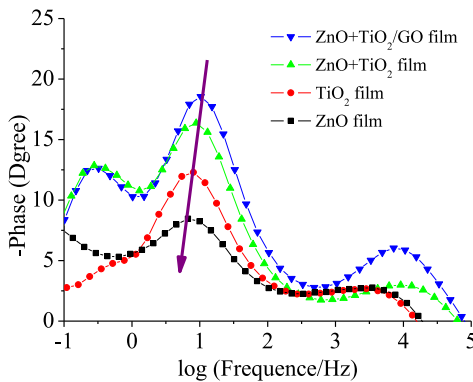


FIGURE 8. The Nyquist plots of DSSCs (a) with different photoanodes and (b) with enlarged view.

In the part of photoanode, GO has high specific surface area and ability of large pores, indicating that the presence of large pores might allow the diffusion of more redox

TABLE 3. The performances of EIS with different photoanodes.

Photoanode	R_s (Ω)	C_1 (μF)	R_1 (Ω)	C_2 (mF)	R_2 (Ω)	τ_e (ms)
ZnO	17.38	1.13	4.26	0.03	987.53	18.01
TiO ₂	13.84	29.55	3.01	2.44	50.42	31.03
ZnO+TiO ₂	13.52	21.83	3.85	4.11	17.81	54.23
ZnO+TiO ₂ /GO	15.73	39.02	1.73	3.00	7.26	68.17

**FIGURE 9.** The bode plots of DSSC fabricated by different structures of photoanode structures.

species inside the pores. Simultaneously, high specific surface area made more N3 dye be adsorbed, which make electrons be collected more effectively. Figure 9 showed the bode plots of DSSC fabricated by different structures of photoanode. According to the Bode phase plots, the electron lifetime (τ_e) could be estimated from the following formula (2) [40].

$$\tau_e = \frac{1}{\omega_{min}} \quad (2)$$

where minimum angular frequency (ω_{min}) is the impedance semicircle at mid-frequencies in the Bode plots. After the modification of GO for DSSC, τ_e of DSSC became longer, which indicated that the decreased recombination of electron with I_3^- ions.

IV. CONCLUSION

In summary, performances of the DSSC with different photoanode structures were investigated. According to the experimental results, the recombination of electron-hole pair and the dark reaction decreased because the ZnO compact layer formed an energy barrier between TiO₂ and FTO substrate. Besides, GO provided a high specific surface area to increase the dye loading and improve the conversion efficiency. Finally, the achieved photovoltaic performances for the DSSC with the structure of TiO₂/GO layer fabricated on the top of ZnO photoanode are 0.72 V of open-circuit voltage, 7.19 mA of short-circuit current density, 61.51 % of fill factor and 3.19 % of conversion efficiency, respectively.

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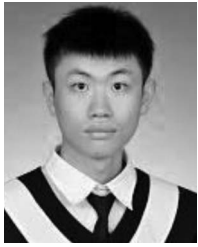


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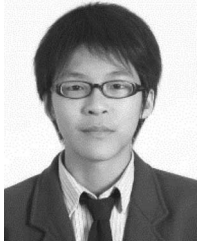
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