# THE CHARACTERIZATION OF DYE-SENSITIZED SOLAR CELL MODIFIED BY REDUCED GRAPHENE OXIDE AND ZrO<sub>2</sub> DOPED TiO<sub>2</sub> NANOFIBERS UNDER T5 FLUORESCENT LAMP

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#### ABSTRACT

Dye-sensitized solar cells (DSSCs) have greater potential for development than other types of solar cells used for indoor lighting. A growing number of studies in the literature have shown that DSSCs exhibit superior photovoltaic conversion efficiency for indoor lighting applications. In this study, we modified a photoanode with TiO<sub>2</sub> nanofibers doped with ZrO<sub>2</sub> and reduced graphene oxide to increase the specific surface area and electron transport capability of the DSSC. Next, we placed the DSSC, which was prepared with commercial titanium dioxide P25, under T5 fluorescent lighting and found that it could achieve a photovoltaic conversion efficiency of 10.37% under T5 fluorescent lighting. When the light intensity was reduced from 1.75 mW/cm<sup>2</sup> to 0.51mW/cm<sup>2</sup>, the photovoltaic efficiency of DSSC prepared with P25 TiO<sub>2</sub> could be increased to 26.63%. When DSSC was modified with TiO<sub>2</sub> nanofibers doped with ZrO<sub>2</sub> and reduced graphene oxide, a photovoltaic conversion efficiency of 18.62% under T5 fluorescent lighting was achieved. When the light intensity was reduced from 1.75 mW/cm<sup>2</sup> to 0.51mW/cm<sup>2</sup>. The overlap of the T5 fluorescence spectrum with the spectrum of dye N719 resulted in effective light absorption, which promoted electron excitation. Our findings confirmed that DSSC exhibits better photovoltaic performance under indoor lighting.

Keywords: Dye-sensitized solar cell (DSSC), reduced graphene oxide, zirconium dioxide, illumination, electrospinning, nanofiber.

## 1. INTRODUCTION

Dye-sensitized solar cells (DSSCs) were first developed in 1991 (O'regan and Grätzeli 1991). Since then, extensive research has been conducted on DSSCs due to their low cost, high stability, colorful appearance, and ease of manufacture (Lee *et al.* 2017; Ahmed *et al.* 2018).

The effective operation of solar cells under indoor illumination has practical significance; for example, they can be used in portable electronic devices and wireless sensing devices. A growing body of evidence indicates that DSSC has a relatively high rate of conversion efficiency under indoor lighting (Freitag *et al.* 2017). Freitag *et al.* (2017) found that DSSC in ambient light was capable of powering electronic devices and extending

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battery life, which suggests that DSSCs have a wide range of applications. Juhász Junger *et al.* (2019) compared DSSC placed under a sunlight simulator or LED light. Although the illumination was the same in both cases (1000W /  $m^2$ ), the same DSSC under LED illumination provided the maximum power. The difference in efficiency can be explained by the difference in the illumination spectra of the two sources.

In this study, we developed a new DSSC, as shown in Fig. 1, and placed it under T5 fluorescent lighting to observe its photovoltaic performances. The structure of this novel DSSC was modified by adding TiO<sub>2</sub> nanofibers doped with ZrO<sub>2</sub> and reduced graphene oxide to the photoanode layer in order to increase the amount of dye adsorption and to improve the electron transport ability. The 1 wt% ZrO<sub>2</sub> and rGO doped TiO<sub>2</sub> nanofibrous photoelectrode with a platinum (Pt) counter electrode shows the best photovoltaic conversion efficiency ( $\eta$ ), and  $\eta$  increased 82% compared to the TiO<sub>2</sub> photoelectrode (Nien *et al.* 2020).

#### 2. EXPERIMENTS

The chemicals used in this study are listed below: titanium dioxide powder (P25, UniRegion Bio-Tech, Taiwan), ruthenium-535-TBA (N719, UniRegion Bio-Tech, Taiwan), acetylacetone (AcAc, Sigma Aldrich, United States), Triton X-100 (PRS Panreac, Spain), titanium (IV) isopropoxide (TiP, Sigma Aldrich, United States), zirconium dichloride oxide (ZrOCl<sub>2</sub> · 8H<sub>2</sub>O, Artikel Germany), citric acid (C<sub>6</sub>H<sub>8</sub>O<sub>7</sub> · H<sub>2</sub>O, Choneye Pure Chemical, Taiwan). Acetic acid (CH<sub>3</sub>COOH, Choneye Pure Chemical, Taiwan) and alcohol (CH<sub>3</sub>CH<sub>2</sub>OH, Choneye Pure Chemical, Taiwan) were used as solvents.

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Fig. 1 Schematic diagram of the DSSC developed in this study

The  $TiO_2$  nanofibers doped with  $ZrO_2$  and reduced graphene oxide were prepared using the electrospinning technique. The photoanode of the DSSC was prepared by the spin coating method and the doctor blade method.

The photoanode was annealed at  $450^{\circ}$ C for 30 minutes in order to enhance the structure of the semiconductor. Then the photoanode was immersed in dye N719 for 24 hours. The upper layer of the platinum counter electrode was covered using a simple packaging technique. Finally, the electrolyte was injected to complete the DSSC sandwich structure. The novel DSSC modified with TiO<sub>2</sub> nanofibers doped with ZrO<sub>2</sub> and reduced graphene oxide is denoted by the abbreviation TZRNF. The DSSC modified with TiO<sub>2</sub> nanofibers doped with ZrO<sub>2</sub> is denoted by the abbreviation TZNF. Hereafter, P25 refers to DSSC prepared with typical P25 nanoparticles.

In order to compare the photovoltaic performances of TZRNF and P25 under indoor lighting, we measured the photovoltaic (PV) parameters of two DSSCs under T5 fluorescent lighting. The light intensity was adjusted by a filter, and the measured light intensities were 1.75 mW/cm<sup>2</sup>, 1.36 mW/cm<sup>2</sup>, 0.85 mW/cm<sup>2</sup>, and 0.51 mW/cm<sup>2</sup>, respectively. The difference in interface resistance between the two DSSCs was measured by electrical impedance spectroscopy (EIS, BioLogic SP-150, France), and the scan frequency for measurement was set from 5 × 10<sup>-2</sup> Hz to 106 Hz, with an amplitude of 10 mV.

### 3. RESULTS AND DISCUSSION

The photovoltaic performances of TZRNF, TZNF, and P25 under a T5 fluorescent lamp were compared. Filters were applied to reduce the light intensity. We used low light intensities of 1.75 mW/cm<sup>2</sup>, 1.36 mW/cm<sup>2</sup>, 0.85 mW/cm<sup>2</sup>, and 0.51 mW/ cm<sup>2</sup>. The photovoltaic performances of the three DSSCs under a T5 fluorescent lamp are shown in Table 1. We found that the photovoltaic conversion efficiency of each device under T5 fluorescent lamp irradiation was significantly improved. The photovoltaic conversion efficiencies of P25, TZNF, and TZRNF under a T5 fluorescent lamp were increased to 10.37%, 17.03%, and 18.62%, respectively. These results can be largely explained by the strong spectral response of the anthraquinone dye to the T5 spectrum. Therefore, the efficiency obtained was higher than that under the solar simulator (Lan et al. 2012). Briefly, the dye N719 used in this study has a light absorption range of about  $400 \sim 800$  nm for visible light absorption (Wang *et al.*) 2004; Gao et al. 2015). This absorption range overlaps with a large portion of the T5 fluorescent lamp spectrum. This demonstrates that DSSC can achieve maximum performance under indoor lighting. In addition, the photovoltaic conversion efficiency of each device showed an increasing tendency as the light intensity decreased from 1.75 mW/cm<sup>2</sup> to 0.17 mW/cm<sup>2</sup>. The higher photovoltaic conversion efficiency of each device at lower light intensities is due to fewer photoelectrons being generated at low light intensities, which thus reduces recombination reactions (Lan et al. 2012). Compared with the results of Freitag et al., who reported a DSSC with a power conversion efficiency of 28.9% under a light source below 1000 lux (Freitag et al. 2017), TZRNF in the present study showed a higher conversion efficiency (over 30%) under a T5 fluorescent lamp with low intensity.

Next, we used a Nyquist diagram to explore the interface impedance of each device under a T5 fluorescent lamp.  $R_1$  generally corresponds to the interface impedance between electrolyte and counter electrode;  $R_2$  corresponds to the interface impedance between photoanode and dye/electrolyte;  $R_s$  represents the interface impedance between the FTO glass and the wire (Chou *et al.* 2018; Dou *et al.* 2011). Figure 2 shows the Nyquist plots and the module circuit diagram of the DSSCs based on P25 photoelectrode under a T5 fluorescent lamp. Figure 3 shows the Nyquist plots and the module circuit diagram of the DSSCs based on TZRNF photoelectrode under a T5 fluorescent lamp.

Intensity (mW/cm <sup>2</sup> )	Material	$V_{OC}(V)$	$J_{SC}$ (mA/cm <sup>2</sup> )	FF (%)	η (%)
1.75	P25	$0.57\pm0.01$	$0.56\pm0.04$	$56.86\pm0.05$	$10.37\pm0.33$
	TZNF	$0.63\pm0.03$	$0.64\pm0.00$	$66.77\pm0.02$	$17.03\pm0.51$
	TZRNF	$0.65\pm0.02$	$0.71\pm0.00$	$70.61\pm0.03$	$18.62\pm0.43$
1.36	P25	$0.57\pm0.01$	$0.52\pm0.01$	$64.03\pm0.02$	$13.95\pm0.76$
	TZNF	$0.63\pm0.03$	$0.64\pm0.00$	$70.14\pm0.00$	$20.79\pm0.54$
	TZRNF	$0.64\pm0.02$	$0.69\pm0.01$	$72.15\pm0.03$	$23.42\pm0.41$
0.85	P25	$0.56\pm0.01$	$0.44\pm0.00$	$64.14\pm0.01$	$18.59\pm0.50$
	TZNF	$0.62\pm0.03$	$0.58\pm0.00$	$71.48\pm0.02$	$30.24\pm0.19$
	TZRNF	$0.63\pm0.03$	$0.65\pm0.02$	$73.03\pm0.02$	$35.18\pm0.55$
0.51	P25	$0.54\pm0.01$	$0.38\pm0.00$	$66.23\pm0.02$	$26.63\pm0.71$
	TZNF	$0.60\pm0.03$	$0.45\pm0.01$	$68.91\pm0.01$	$36.48\pm0.17$
	TZRNF	$0.60\pm0.03$	$0.54\pm0.02$	$73.97\pm0.00$	$46.99\pm0.48$

Table 1 The photovoltaic parameters of dsscs based on various photoanodes under t5 fluorescent lamp.

Table 2 shows that the RS value was generally stable, indicating that the light intensity did not affect the RS. In addition, under the irradiation of the T5 fluorescent lamp, as the light intensity decreased from  $1.75 \text{ mW/cm}^2$  to  $0.17 \text{ mW/ cm}^2$ , the R<sub>2</sub> values of both devices increased. This phenomenon can be attributed to the decrease in the amount of photo-generated electrons due to the decrease in light intensity, which reduces the possibility of photo-generated electrons recombining with holes in the electrolyte, resulting in increases in R<sub>2</sub> and R<sub>1</sub>.



Fig. 2 Nyquist plots and module circuit diagram of the DSSCs based on P25 photoelectrode under a T5 fluorescent lamp



Fig. 3 Nyquist plots and module circuit diagram of the DSSCs based on TZRNF photoelectrode under a T5 fluorescent lamp

 Table 2
 The impedance parameters of the dsscs based on various photoanodes under a T5 fluorescent lamp.

Light intensity (mW/cm <sup>2</sup> )	Photoelectrode	$\mathrm{Rs}\left(\Omega\right)$	$R_1(\Omega)$	$R_2(\Omega)$
1.75	P25	5.18	19.23	68.72
	TZRNF	3.11	10.12	35.55
1.20	P25	5.11	19.48	97.63
1.30	TZRNF	3.23	10.48	37.62
0.95	P25	6.17	19.91	109.8
0.85	TZRNF	3.05	11.39	41.43
0.51	P25	5.87	19.99	132.1
0.51	TZRNF	3.33	11.44	48.64

#### 4. CONCLUSIONS

We developed a novel dye-sensitized solar cell modified with TiO<sub>2</sub> nanofibers doped with ZrO<sub>2</sub> and reduced graphene oxide, which achieved a photovoltaic conversion efficiency of 18.62% when illuminated by a T5 fluorescent lamp. This effect can be largely explained by the strong spectral response of the anthraquinone dye to the T5 spectrum. When the light intensity was reduced from 1.75mW/cm<sup>2</sup> to 0.51mW/cm<sup>2</sup>, the photovoltaic conversion efficiency reached 46.99%. The higher photovoltaic conversion efficiency at lower light intensities was due to the decrease in photoelectrons generated at low light intensities, which in turn reduced the recombination reactions.

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