

## SYNTHESIS, CHARACTERISATION, AND FABRICATION HOLLOW FIBRES OF Zn-DOPED TiO<sub>2</sub> FOR DYE-SENSITIZED SOLAR CELLS

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### Abstract

The study aims to synthesize and characterize the hollow fibres of Zn-doped TiO<sub>2</sub>. The hollow fibres were synthesized using a co-axial electrospinning machine where the sheath and core solution were composed of titanium (IV) isopropoxide and olive oil, respectively. Doping Zn was conducted by using zinc nitrate hexahydrate solution. The green fibres were then sintered at a temperature of 500°C. Subsequently, the hollow fibres of Zn-doped TiO<sub>2</sub> were fabricated as working electrode for dye-sensitized solar cells (DSSCs). The scanning electron microscopy images and X-ray diffraction analysis show that doping Zn produced the larger diameter and tuned the fraction of anatase and rutile of the hollow fibres of Zn-doped TiO<sub>2</sub>. The best performance of DSSCs occurred at doping Zn into TiO<sub>2</sub> with a weight ratio of 0.4% where the respective open circuit voltage, current density, fill factor, and efficiency were 0.612 V, 2.935 mA/cm<sup>2</sup>, 49.55%, and 0.89%. The main role of doping Zn into hollow fibres of TiO<sub>2</sub> for enhancing the performance of DSSCs was by increasing the current density caused by the larger diameter of hollow fibres of TiO<sub>2</sub> for dye loading and synergistic effect of anatase and rutile in the hollow fibres of TiO<sub>2</sub> for staging the electrons transfer.

Keywords: Hollow fibres, Co-axial electrospinning, Zn-doped TiO<sub>2</sub>, Dye-sensitized solar cell.

**Nomenclatures**

$B$	Full width at half maximum, FWHM (rad)
$D$	Crystalline diameter (nm)
$FF$	Fill factor
$IA$	X-ray integrated intensities of the reflection of the anatase
$I_{MPP}$	Maximum power point current (mA)
$IR$	X-ray integrated intensities of the reflection of the rutile
$I_{SC}$	Short circuit current (mA)
$J_{SC}$	Short circuit current density (mA/cm <sup>2</sup> )
$k$	Scherrer's constant, 0.9
$V_{MPP}$	Maximum power point voltage (V)
$V_{OC}$	Open circuit voltage (V)
$X$	Weight fraction of rutile (%)

**Greek Symbols**

$\lambda$	Wavelength of X-ray (1.5406 Å)
$\theta$	Bragg angle (°)
$\eta$	Efficiency

**Abbreviations**

BET	Brunauer, Emmett and Teller
DSSCs	Dye-sensitized solar cells
FTO	Fluorine-doped tin oxide
SEM	Scanning electron microscopy
TiO <sub>2</sub>	Titanium dioxide
TTIP	Titanium (IV) isopropoxide
TEM	Transmission electron microscopy
XRD	X-ray diffraction
Zn	Zinc
ZnO	Zinc oxide

**1. Introduction**

Dye sensitized solar cells (DSSCs) are the promising device for harvesting the solar energy because their operational cost is low and their performance is good enough when compared with solid-state photovoltaics. Although the operating principle of DSSCs is well understood, enhancing their performance is not an easy task since it is mutually influenced by many factors. Nowadays, various methods have been developed for exploring the knowledge of how to improve the performance of DSSCs. One of the important roles is using nano-sized semiconductor materials, particularly from anatase TiO<sub>2</sub> since they can produce a higher energy conversion efficiency when compared with that from rutile TiO<sub>2</sub> [1].

Furthermore, another method is carried out by producing a greater current density from DSSCs by means of simplifying and streamlining the movement of electrons. To do so, it used single-crystalline semiconductor nanowires, nanofibres, nanotubes arrays, and core-shell structure [2]. Of the various proposed strategies, nanofibres-shaped semiconductors produced via electrospinning are very fascinating because of the ease of fabrication process with low cost [3 - 5].

Moreover, the repeatability and reproducibility of the fibres synthesized from the electrospinning machine was acceptable for the requirement of mass production [6]. Main parameters influencing the shape and the diameter of the nanofibres synthesized by electrospinning machine are solution concentration, solution viscosity, solution conductivity, molecular weight, solution rate, capillary size, working distance, and applied voltage [4, 7-11].

Interestingly again, the nanofibres semiconductor for DSSCs can be made in the form of a hollow to increase the dye uptake by using two coaxial capillaries electrospinning [12]. The solution used at the centre of the coaxial needle must have a lower volatility than that of the solution used at the outer side. The process of the formation of hollow fibres occurs by means of removing the core material by heating [13]. The hollow fibres are predicted to have a large surface area for increasing dyes adsorption onto TiO<sub>2</sub> semiconductors.

Furthermore, the goal of the semiconductor synthesizing does not only for improving the appropriate morphology but for increasing the electrical properties also. One of the methods to achieve such goal is using doping. Nitrogen and ytterbium doped into TiO<sub>2</sub> increased dipole moments and improved the photocatalytic activity of TiO<sub>2</sub> [14]. Meanwhile, the doping of N-Zn producing 10-13 nm-sized TiO<sub>2</sub> particles improved the efficiency of the DSSCs to 2.6% [15]. The Fe doping at 0.28 wt% into the anatase TiO<sub>2</sub> has caused a partially shift of anatase TiO<sub>2</sub> (E<sub>b</sub> = 3.0-3.1 eV) into rutile (E<sub>b</sub> = 3.2 to 3.3 eV) [16]. Moreover, TiO<sub>2</sub> photo anode doped with Niobium (Nb) at 1 mol% showed a highest photovoltaic efficiency because they possessed the best band structure for DSSCs compared with that of vanadium (V)- and tantalum (Ta)-doped TiO<sub>2</sub> [17]. Furthermore, the 0.5 mol% ZnO-covered TiO<sub>2</sub> film possesses more outstanding ability to transport electrons leading to an increase of solar cells efficiency by 27.3% when compared with that of the pure TiO<sub>2</sub> (anatase) film [18]. The doping of magnesium into anatase TiO<sub>2</sub> has shifted the Fermi level 1 eV to a negative energy leading to increase the  $J_{sc}$  but to decrease the  $V_{oc}$  [19]. Meanwhile, the increase of TiO<sub>2</sub> electron mobility was maximum when doped by Zn of 0.1 mol% [20]. The aforementioned methods shows that the properties of the TiO<sub>2</sub> semiconductor resulted by doping are strongly depended by the type and concentration of dopant materials. The role for increasing electrical properties and enhancing the performance of DSSCs is mainly by means of enhancing the current density rather than voltage. To this point of view, the Zn doping is interesting because it did not may control the TiO<sub>2</sub> particles size but increase the electron mobility also. Unfortunately, there are still limited studies of the employing Zn doping into TiO<sub>2</sub> hollow fibres for DSSCs. Therefore, we report here the synthesis and characterization of Zn-doped TiO<sub>2</sub> hollow fibres for improving the performance of the DSSCs.

## 2. Experimental Procedures

### 2.1. Synthesis and characterization of hollow fibres TiO<sub>2</sub> semiconductor

TiO<sub>2</sub> semiconductors were synthesized from the materials of titanium (IV) isopropoxide (TTIP, 99.9%, Sigma Aldrich-377996), polyvinylpyrrolidone (PVP, MW 40,000, Merck-PVP40), acetic acid (99.7%, Sigma Aldrich-320099), absolute ethanol (99.5%, Sigma Aldrich-459844). The materials were used

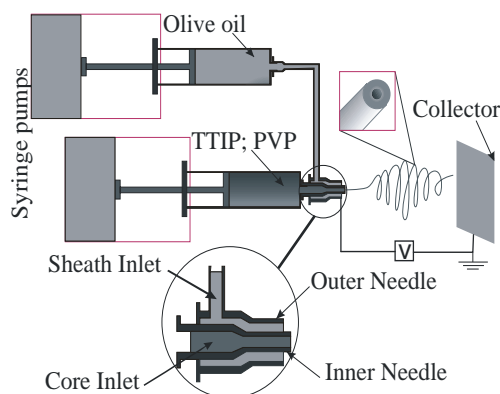
without further purification. To prepare the precursor solution of electrospinning [21], 0.37 g of TTIP, 1.13 g of PVP, and 2 g of ethanol were mixed and stirred for 1 h. The acetic acid (0.78 g) was poured into the previous solution and then stirred for 11 h until transparency.

To prepare the solution for synthesizing the Zn-doped TiO<sub>2</sub>, zinc nitrate hexahydrate (98%, Sigma Aldrich-228737) and acetic acid (0.78 g) were mixed and stirred for 12 h. The weight ratio between Zn and TiO<sub>2</sub> was controlled at 0.1, 0.4, 0.7, and 1.0%. Finally, the un-doped TTIP solution and the doped TTIP solution were ready for electrospinning.

To prepare the precursor solution for inner side (core) of hollow fibres, the olive oil (Sigma Aldrich-O1514) was stirred and heated at the temperature of 150°C by using magnetic stirrer for 4 h. This treatment was used for reducing the moisture content in the olive oil. The solution was then allowed to stand at a temperature of 25°C for 25 h until the foam and voids disappeared. Therefore, the olive oil solution was ready for electrospinning.

Synthesizing the fibres of TiO<sub>2</sub> was conducted by electrospinning machine showed in Fig. 1. The TTIP solution approximately 1 ml was put in the sheath of syringe pump. Meanwhile, the olive oil solution of 1 ml was poured into the core of syringe pump. The respective diameter of the core and the sheath needle is 0.3 mm and 0.8 mm. The needle of syringe pump and the FTO (fluorine-doped tin oxide) glass were then connected to the positive and the negative terminal of the high voltage, respectively. The distance between the tip of the syringe pump needle and the FTO glass was 29.5 cm, horizontally. The TTIP and olive oil solutions were then pushed out at a flow rate of 0.6 ml/h and 0.2 ml/h, respectively. When the electrospinning machine was subjected to a high voltage charge of approximately 15 kV, the solutions were then attracted by electrostatic fields towards the FTO glass. Firstly, the solutions were firstly formed into Taylor cone shape, followed by spinning into fibres shape, and finally the fibres attached on the surface of the collector called as green fibres.

The green fibres were then sintered at a temperature of 500°C for 2 h with a heating rate of 2.5°C/min. The hollow fibres of TiO<sub>2</sub> were produced when the solution of olive oil evaporated and the TTIP solution crystallized into TiO<sub>2</sub>. Another objective of the sintering process was to decompose most of the organic materials including PVP and acetic acid.



**Fig. 1. Scheme of co-axial electrospinning machine.**

The morphological features of the hollow TiO<sub>2</sub> fibres were examined using scanning electron microscopy (SEM, FEI: Inspect-S50). Phase analyses were carried out using X-ray Diffraction (XRD, Rigaku) with Cu-K $\alpha$  radiation in the range of 20°-80° (2 $\theta$ ).

## 2.2. Fabricating and testing of DSSCs

To fabricate the DSSCs, fluorine-doped tin oxide (FTO) conducting glass substrates were first prepared using spray pyrolysis [22, 23]. Tin (II) chloride dihydrate (16.116 g, Cl<sub>2</sub>Sn\*2H<sub>2</sub>O, Merck), ammonium fluoride (0.265 g, NH<sub>4</sub>F, Merck), and ethyl alcohol (100 mL, 96%, Merck) were mixed and sprayed on the glass surface followed by heating at 450°C with a heating rate of 4°C/min.

To prepare the catalytic platinum counter electrode, the FTO glass was first heated at 200°C. Platinum was then chemically deposited, from a 5 mM H<sub>2</sub>PtCl<sub>6</sub> solution (Merck), onto the FTO glass followed by heating at 300°C and subsequent cooling with a cooling rate of 1°C/min. [24, 25].

To prepare the working electrode, the sintered hollow TiO<sub>2</sub> fibres were coated onto the FTO glass (1 cm  $\times$  1 cm) by the method of doctor blade. The resulting film-coated FTO glass was sintered at 450°C for 2 h [26, 27] to strongly adhere the hollow TiO<sub>2</sub> fibres onto the FTO glass [27, 28]. The thickness of the TiO<sub>2</sub> semiconductor film was maintained at 20  $\mu$ m.

The electrolyte solution employed in the DSSCs was prepared as such: sodium iodide (3.30 g, 99.95%, Merck) was dissolved in 30 mL acetonitrile under stirring for 15 min, prior to adding iodine (523.88 g, 99.95%, Merck) and tungstophosphoric acid hydrate (5.48 mg, H<sub>3</sub>O<sub>40</sub>PW<sub>12</sub>·xH<sub>2</sub>O, Merck). Stirring was continued for 24 h to achieve a homogeneous solution. The electrolyte solution was then injected into the assembled DSSCs spaced at 50  $\mu$ m and then sealed. The voltage and current of DSSCs were recorded on a Keithley 2602A meter (USA) under illumination using a lamp of 1000 W/m<sup>2</sup>. The fill factor and efficiency of the DSSC was determined from the open circuit voltage ( $V_{OC}$ ), the short circuit current ( $J_{SC}$ ), the maximum power point voltage ( $V_{MPP}$ ), and the maximum power point current ( $I_{MPP}$ ) as below.

$$FF = \frac{V_{MPP} \times I_{MPP}}{V_{OC} \times I_{SC}} \quad (1)$$

$$\eta = \frac{V_{MPP} \times I_{MPP}}{I_{light} \times A} \quad (2)$$

## 3. Results and Discussion

### 3.1. XRD characterization of Zn-doped hollow TiO<sub>2</sub> fibres

Figure 2 shows the X-ray diffraction pattern of Zn-doped TiO<sub>2</sub>. The peaks were detected at 2 $\theta$  of 25.4°, 37.9°, 48.1°, 53.8°, and 55.0° assigned to the (101), (004), (200), (105), and (211) lattice planes corresponding to the TiO<sub>2</sub>. The highest peak of 25.4° (101) and 27.5° (110) showed the TiO<sub>2</sub> anatase and the TiO<sub>2</sub> rutile phase,

respectively. Furthermore, the amount of anatase and rutile was calculated using the following equation [29, 30]:

$$X = \left(1 + 0.8 \frac{IA}{IR}\right)^{-1} \quad (3)$$

Where,  $X$  is the weight fraction of rutile.  $IA$  and  $IR$  are the X-ray integrated intensities of the reflection of the anatase (101) and rutile (110). There are no ZnO diffraction peaks in the XRD spectra when Zn was doped at a weight ratio of Zn/TiO<sub>2</sub> up to 0.7% indicating that doping elements were well dispersed in TiO<sub>2</sub>. At a weight ratio of Zn/TiO<sub>2</sub> of 1.0%, the ZnO diffraction peak was detected.

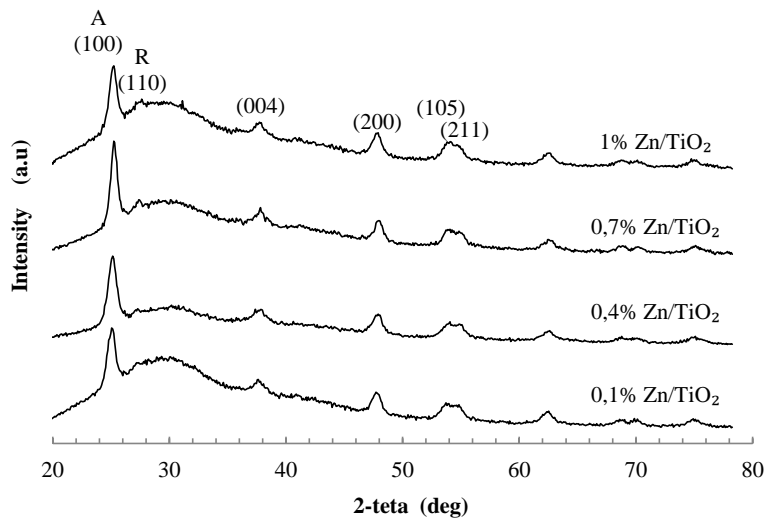


Fig. 2. X-ray diffraction pattern of Zn-doped TiO<sub>2</sub>.

The diameter of crystallite hollow TiO<sub>2</sub> fibres was calculated by using Debye-Scherrer's equation based on the highest peak of  $2\theta$  at 25.4° [31]:

$$D = \frac{k \cdot \lambda}{B \cdot \cos \theta} \quad (4)$$

where  $D$  is the diameter of the crystallite TiO<sub>2</sub>.  $\lambda$  is the wavelength of X-ray radiation (Cu K $\alpha$  = 0.15406 nm).  $k$  is constant that is considered 0.9.  $\theta$  is the angle of diffraction.  $B$  is the full width at the half-maximum intensity.

The crystallite diameter and the composition of anatase and rutile are shown in Table 1. The crystallite diameter of hollow TiO<sub>2</sub> fibres was varying from 8.07 to 10.41 nm. The main influence of Zn doping on the crystallite quality of hollow TiO<sub>2</sub> fibres was change the composition of the anatase and rutile phase. The highest weight fraction of anatase phase was 91% found at Zn/TiO<sub>2</sub> of 0.4%. Above 0.4%, the fraction of anatase was significantly reduced.

Meanwhile, the band gap of hollow TiO<sub>2</sub> fibres calculated by Kubelka-Munk theory [32] was 3.24 eV to 3.25 eV. The Zn doping up to a weight ratio of 1.0% did not significantly change the band gap energy of hollow TiO<sub>2</sub> fibres. The band

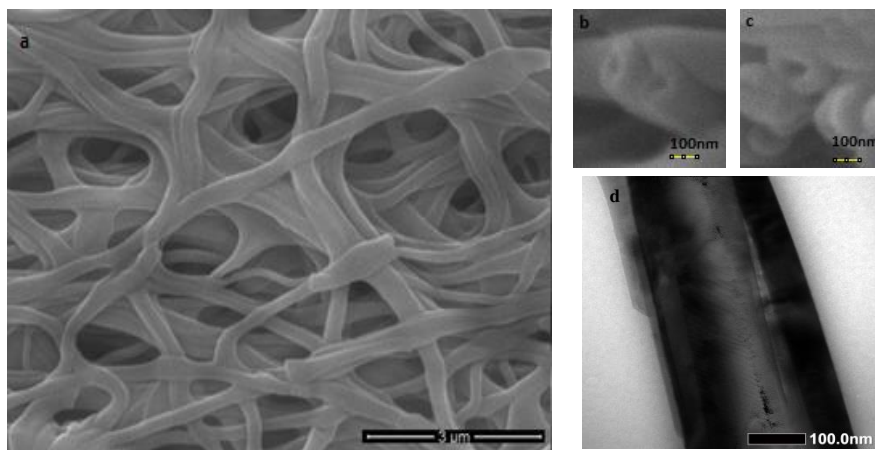
gap energy of hollow TiO<sub>2</sub> fibres was close to the previous study for hollow TiO<sub>2</sub> fibres, namely 3.21 [33].

**Table 1. The band gap energy and crystallite quality of hollow TiO<sub>2</sub> fibres.**

Weight ratio of Zn/TiO <sub>2</sub> (%)	Band gap energy (eV)	Crystallite diameter (nm)	Composition (%)	
			Anatase	Rutile
0.1	3.24	8.99	84	16
0.4	3.24	8.07	91	9
0.7	3.25	10.41	86	14
1.0	3.25	9.40	82	18

### 3.2. Morphology of hollow fibres of Zn-doped TiO<sub>2</sub>

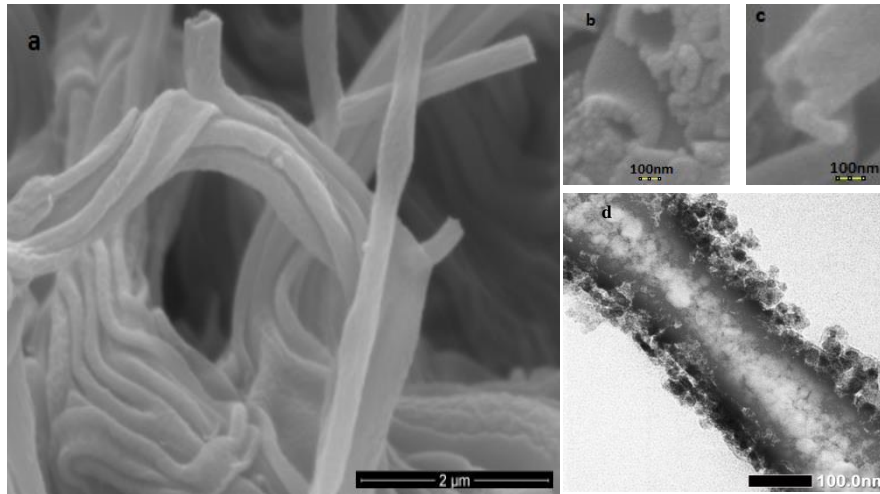
Figure 3 shows the morphology and size of hollow fibres TiO<sub>2</sub> after sintering at a temperature of 500°C for 2 h. The structures of hollow fibres are continuously connected without cracking. The size of the outer diameter of the hollow fibres was ranging from 192 nm to 314 nm, with an average fibre diameter of 221 nm. Meanwhile, the inner diameter of hollow fibres is not uniform ranging from 39 nm to 85 nm, with an average diameter of 65 nm.



**Fig. 3. SEM images of TiO<sub>2</sub> hollow fibres synthesized by coaxial electrospinning process followed by sintering at a temperature of 500°C for 2 h. (a) top view; (b) and (c) cross section; (d) TEM image.**

Meanwhile, Fig. 4 shows that the morphology and size of Zn-doped TiO<sub>2</sub> hollow fibres after sintering at a temperature of 500°C for 2 h. The structure of the fibres is continuously connected without cracking. The size of the outer diameter of the hollow fibres is ranging from 245 nm to 328 nm, with an average diameter of 285 nm. Furthermore, the diameter of hollow fibres is not uniform, with hole sizes are ranging from 44 nm to 139 nm, with an average diameter of 91 nm. Thus, doping Zn into TiO<sub>2</sub> caused the increase of fibres diameter because the diameter of Zn<sup>2+</sup> is larger than that of Ti<sup>4+</sup>. Therefore, Zn is difficult to dope into

the internal lattice of  $\text{TiO}_2$  and forms Ti-O-Zn on the interface of the crystal  $\text{TiO}_2$  [15]. This phenomenon was noted also by X-ray diffraction spectrum in Fig. 2 that the doping of Zn at 1% formed new phase of ZnO.



**Fig. 4.** SEM images of Zn-doped  $\text{TiO}_2$  hollow fibres synthesized by coaxial electrospinning process followed by sintering at a temperature of  $500^\circ\text{C}$  for 2 h. (a) top view; (b) and (c) cross section; (d) TEM image.

### 3.3. Performance of DSSCs

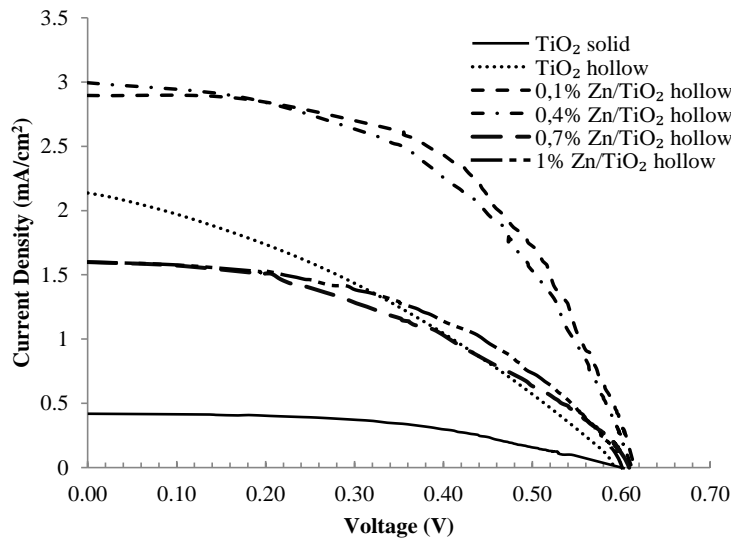
Figure 5 shows the photocurrent-voltage curve of DSSCs based on the hollow fibres of Zn-doped  $\text{TiO}_2$  under irradiation intensity of  $100 \text{ mW/cm}^2$ , with the cell performances summarized in Table 2. The efficiency of the DSSC fabricated from the hollow and the solid  $\text{TiO}_2$  fibres was 0.44% and 0.13%, respectively. The hollow fibres were capable to increase the efficiency of DSSCs up to four times when compared with that of the solid fibre-based DSSC. This significant increment of the efficiency in the hollow  $\text{TiO}_2$  fibres-based DSSC was mainly caused by pores radius size and surface area. The hollow fibres of  $\text{TiO}_2$  have a higher pores radius size and surface area than that of solid fibres of  $\text{TiO}_2$ . The respective pores radius size of solid and hollow  $\text{TiO}_2$  fibres was 1.754 and 2.261 Å. BET measurement test results that the surface areas of  $\text{TiO}_2$  solid fibres,  $\text{TiO}_2$  hollow fibres and Zn-doped  $\text{TiO}_2$  hollow fibres were 43.75, 65.95 and 86.75  $\text{m}^2/\text{g}$ , respectively. Zn Doping on  $\text{TiO}_2$  hollow fibres increase the value of the porosity of approximately 24% compared with  $\text{TiO}_2$  hollow fibres without doping. The BET analysis of solid fibres found from this study was higher than that from the previous study (15.2  $\text{m}^2/\text{g}$ ) [34].

Table 2 shows also that the DSSCs with Zn-doped  $\text{TiO}_2$  semiconductors produced similar  $V_{OC}$  approximately between 0.592 and 0.615 V. However, the  $J_{SC}$  of the DSSCs fabricated from Zn-doped  $\text{TiO}_2$  was significantly influenced by Zn doping. The amount of  $J_{SC}$  and efficiency of DSSCs increased up to two fold when  $\text{TiO}_2$  was doped by Zn up to the weight ratio of 0.4%. Over 0.4%, the



amount of  $J_{SC}$  and efficiency of DSSCs experienced a sharp decline. Therefore, the optimum performance of DSSCs occurred by doping Zn into  $TiO_2$  with a weight ratio of 0.4% where the respective  $V_{OC}$ ,  $J_{SC}$ ,  $FF$ , and efficiency were 0.612 V, 2.935 mA/cm<sup>2</sup>, 49.55%, and 0.89%. This performance of DSSCs was higher than the previous study of DSSCs based on ZnO nanowires and N3 dye where  $V_{OC}$ ,  $J_{SC}$ , and  $FF$  were 0.612 V, 1.029 mA, and 22.6% [35].

Therefore, the role of Zn doped into  $TiO_2$  in improving the performance of solar cells occurred primarily by the improving the current density because Zn doping might increase the electron mobility [20]. In addition, the Zn doped into  $TiO_2$  increasing the hole diameter of fibres in section 3.2 caused the increase the dye loading in the semiconductors. The Zn doping tuned also the fraction of anatase found in the hollow  $TiO_2$  fibres as discussed in section 3.1. The optimum performance of DSSCs occurring with Zn doping at 0.4% indicated that there is a synergistic effect of anatase and rutile in the  $TiO_2$  semiconductors for enhancing the performance of DSSCs. The anatase possesses an indirect band gap semiconductor. In the indirect band gap material, the minimum in the conduction band is away from the maximum in the valence band. This enables the excited electron to stabilize at the lower level in the conduction band. Because the properties of indirect band gap material, so that it minimizes the recombination effect in DSSCs [36]. This results were consistent with the previous study that the strongest synergistic effect between the anatase and rutile phases occurred in the DSSCs with rutile fraction of 13 wt% [1]. At this fraction of rutile, the staging of band gap energy between anatase and rutile was the best and caused the easier transfer of electrons from rutile to anatase in DSSCs. The indirect band gap enables the excited electron to stabilize at the lower level in the conduction band itself leading to its longer life and greater mobility [36]. Further addition of rutile might trigger accelerated interception of injected electrons by the electrolyte, resulting in decreased current density and photo voltage [1].



**Fig. 5. The photocurrent-voltage curve of DSSCs under irradiation intensity of 100 mW/cm<sup>2</sup>**

**Table 2. The performance of DSSCs**

Weight ratio of Zn/TiO <sub>2</sub> (%)	Fibres	V <sub>OC</sub> (V)	J <sub>SC</sub> (mA/cm <sup>2</sup> )	FF (%)	η (%)
0	Solid	0.604	0.419	51.39	0.13
0	Hollow	0.592	2.136	34.61	0.44
0.1	Hollow	0.615	2.506	55.56	0.86
0.4	Hollow	0.612	2.935	49.55	0.89
0.7	Hollow	0.609	1.599	42.90	0.42
1.0	Hollow	0.601	1.384	47.80	0.40

#### 4. Conclusions

The method of fabricating hollow TiO<sub>2</sub> fibres semiconductor and Zn doping into TiO<sub>2</sub> fibres by using coaxial electrospinning has been successfully carried out. The Zn doping produced the larger diameter of hollow TiO<sub>2</sub> fibres. In addition, the Zn doping has tuned the fraction of anatase and rutile in the hollow fibres of TiO<sub>2</sub>. In contrast, the Zn doping did not significantly change the crystallite diameter and band gap energy. The best performance of DSSCs occurred by doping Zn into TiO<sub>2</sub> with a weight ratio of 0.4% where the respective V<sub>OC</sub>, J<sub>SC</sub>, FF, and efficiency were 0.612 V, 2.935 mA/cm<sup>2</sup>, 49.55%, and 0.89%. The main role of Zn doping into hollow TiO<sub>2</sub> fibres for enhancing the performance of DSSCs was by increasing the current density caused by the larger diameter of hollow TiO<sub>2</sub> fibres for dye loading and the synergistic of anatase and rutile in the hollow TiO<sub>2</sub> fibres for staging the electrons transfer. Further study is needed to optimize the surface area and the diameter of hollow TiO<sub>2</sub> fibres for DSSCs by tuning the flow rate of core and sheath solutions in the electrospinning. It is interesting also to study further the method of synthesizing the uniform fibres from the electrospinning.

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