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Increasing the Efficiency Significantly of Dye-Sensitized Solar Cells based on ZnO Nanomaterial Photoanode by Doping Titanium

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This work was conducted for fabrication of Dye Sensitized Solar Cells (DSSC) based on ZnO nanomaterials as photoanode and Titanium (Ti) as a dopant material. The aims of this research are to see the effect of adding Ti to ZnO materials on optical, structural, morphological properties and on the efficiency of DSSC based on ZnO. The novelty of this work is the tunable properties of ZnO by varying Ti concentration (0.02 M, 0.04 M and 0.06 M). The properties of ZnO have been analyzed using spectroscopy UV-Vis, X-ray diffraction (XRD), field emission scanning electron microscope (FESEM), and energy dispersive X-ray(EDX). The power conversion efficiency (PCE) of the DSSC was recorded from 0.58% to 2.19%

Keywords: DSSC; ZnO; Metal Transition; Titanium

1 Introduction

Fossil fuels as one of energy sources are non-renewable energy and they have been used in several centuries. Since several years, the reserve of fossil fuels have become critically limited. To overcome these problems, it is necessary to find an alternative replacements using renewable energy such as air, water, sunlight and etc. Solar energy is the promising alternate due to clean, environmental friendly, low cost production and available free in most countries[1-2]. The important of solar cells is an abundant source so that suitable for uses as renewable and sustainable energy in the future.

Dye sensitized solar cells (DSSCs) as a third generation of solar cell technology was proposed by by O'Regan & Grätzel[3]. DSSCs is a promising alternate for renewable energy, due to it is work very well under artificial and diffuse-light condition[4], low-cost, easy to fabricate, fast assembling process and low toxicity[5]. Fig. 1 shows the DSSC components consisting of transparent conducting oxide (TCO), working electrode/photoanode, electrolyte, dye as a sensitizer, and counter electrode. The photoanode of DSSC usually using TiO_2 and ZnO, because of their good semiconductor properties. The ZnO materials have been choosen as an active material due to their simple preparation[6]. ZnO has been explored for any applications such as photovoltaic, sensing and photocatality[7].

As a result, ZnO has large binding exciton energy and has a band gap energy of 3,37 eV in room temperature. However, the performance of DSSCs based on ZnO has still low conversion energy efficiency of approximately 0,4% to 5,8%[8]. In order to increase the performance of DSSC based on ZnO, several researchers have carried out study such as morphology, thickness, particle size of ZnO, or adding an element to the ZnO structure by that the performance will increase.

One of the method to increase the optic properties and physics properties of ZnO is dope with metal. The main propose of doping is not only to optimize the band gap but also to modify the electrical properties[9]. In recent years, DSSCs which fabricate with doped ZnO have been studied. The studies on the performance of DSSCs fabricated with ZnO doped such as Li[9], Sr[10] & Eu[11]. Some researchers has studied about doped ZnO with metal transition (TM) because

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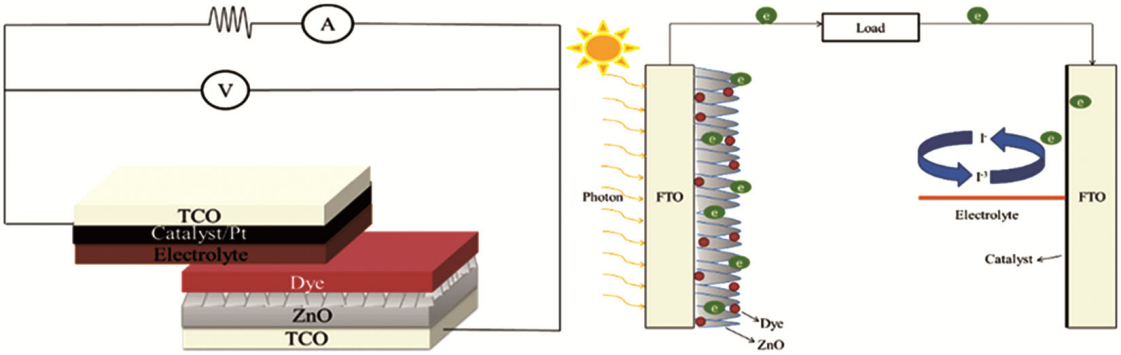

Fig. 1 — Sandwich structure and schematic diagram or working principle of DSSC.

of it is potential uses in spintronic applications due to room temperature ferromagnetism (RTFM)[12]. Titanium (Ti) as a transition metal has an attractive material as a dopant. Ti^{4+} and Zn^{2+} it is have two electron valences, thus Ti can be grant more than 1 electron[12]. Previous researcher[13] have studied ZnO doped with Ti which produces efficiency 5,56%.

2 Experimental Method

2.1 Synthesis Method

This project was synthesis using seed mediated hydrothermal method which divided in two steps. The first step is seeding that dissolved Zinc Acetate Dehydrate (ZAD) 0.1 M in ethanol 10 ml and put into ultrasonic bath for five minutes. The next step is growth which is used 0.2 M Zinc Acetate Hexahydrate (ZNH) as a precursor and 0.1 M Hexamethylenetetramine (HMT) as a surfactant, each of which is dissolved in 10 ml DI water. For doping material using Titanium IV Isopropoxide which vary the concentration of 0.02 M, 0.04 M and 0.06 M. The growth process was in oven with temperature 90 ℃ for 8 hours.

2.2 Material Characterization and Performance Checking of DSSC

The optical properties of samples was analyzed using UV-Vis characterization which type spectrophotometer UV-1800 Shimadzu. For crystalinity properties this project used X-Ray diffraction X'Pert[3] Powder. The physical properties of samples was analyzed using field emission scanning electron microscope (FESEM) with type JEOL JSM-7600 F and energy dispersive x-ray was used for analyzed the contents of an element from sample which has type X-Max Oxford. The performance of DSSC was analyzed using Keithly 2430 Source Meter.

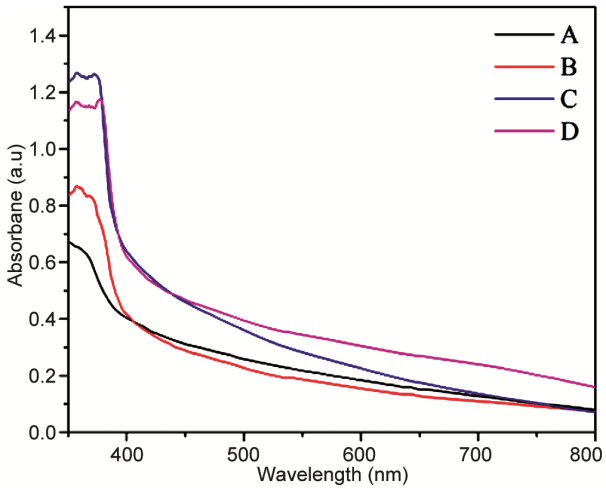

Fig. 2 — UV-Vis absorption spectrum of the sample (a) ZnO, (b) ZnOTi 0.02 M, (c) ZnOTi 0.04 M and (d) ZnOTi 0.06 M.

3 Results and Discussions

3.1 UV-Vis Analysis

The optical properties of ZnO doped with Ti was shown if Fig. 2. In the Figure shows that strong absorption occur in the wavelength range 300-370 nm which can observed that the strong absorption in UV and visible spectrum and the results of this study are in accordance with results Kanmani[12]. In the absorption spectrum range, it can be indicate that the ZnO that grows has the characteristics of wurtztie hexagonal[14]. It can be seen in Fig. 2 that as the Ti concentration increases, the absorption will decrease. The highest absorption occur in ZnO doped Ti 0.04 M and it can make an assumption that Ti with concentration 0.04 M has a high density. The impact of the increased density is an increase in photon absorption of photons in the sample. The increasing concentration of Ti causes sample to be less transparent, by that more ZnO molecules are involved in the light absorption process[15].

In Fig. 3 band gap energy has been calculated using Taucplot equation[16]:

$$(\alpha h\upsilon)^2 = A\,(h\upsilon - Eg) \quad ...(1)$$

Where α is the absorption coefficient and a plot $(\alpha h\upsilon)^2$ the function of$h\upsilon$ was made to determine Eg by linear fitting. The observed band gap are listed in Table 1. Based on band gap energy results atomic doping causes a decrease in band gap energy. The higher concentration of Ti, will make band gap more decrease. An extrapolation of Tauc Plot the absorption edges shift towards to the higher wavelength (red shifted) with the addition of Ti[13].

3.2 XRD Analysis

The diffraction spectrum shown in Fig. 4, it shows that the sample formed is crystalline which is characterized by sharp diffraction peaks. The Figure shows five diffraction peaks at an angle of 2θ 31.77°, 34.43°, 36.36°, 47.55° and 56.61° with strongest line in angle 2θ = 36.26°. Software analysis described the diffraction peaks according to the crystal plane (010), (002), (011), (012) and (110) which are indexed to wurtzite hexagonal ZnO material. The diffraction peaks occur in the plane of crystal orientation (011).

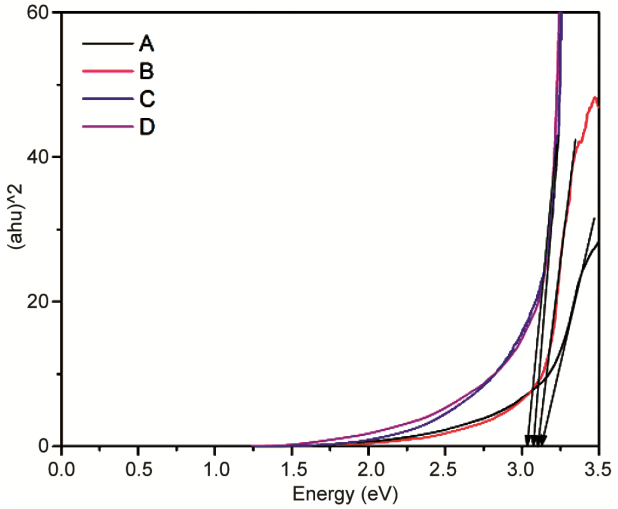

Fig. 3 — Band gap energy from sample (a) ZnO, (b) ZnOTi 0.02 M, (c) ZnOTi 0.04 M and (d) ZnOTi 0.06 M.

Tabel 1 — Band gap energy of the sample

Sample	Energy (eV)
ZnO	3.12
ZnO:Ti0.02 M	3.10
ZnO:Ti0.04 M	3.07
ZnO:Ti0.06 M	3.03

This peak orientation (011) indicates that pure ZnO and ZnO doped with Ti are in the xy-plane, it is not perpendicular to the substrate[17].

The average of crystallite size can be calculated using Debye-Scherrer equation [13]:

$$D_v = \frac{K\lambda}{\beta \cos\theta} \quad ...(2)$$

The results of these calculation will be shown in Table 2. It can be seen that the FWHM value of ZnO increased after being doped with Ti, indicating a decrease in crystallinity. This is caused by the Ti atom can be replaced the position of Zn atom substitutionally. The difference in ionic radius between Zn and Ti causes a mismatch which causes micro-stresses to appear on the crystal structure[18]. Can be observed in the Table 2 the lowest FWHM value in Ti concentration 0.04 Mwhich is 0.29 and crystal size is 31.46 nm.

The shifted of the XRD peak in plane orientation (011) is shown in Fig. 5 but it is not clearly observed due to the shift value is very small, so it can be seen in Table 3.

It can be seen in the Table 3 that slightly shifting of the peaks to the higher angles for ZnO doped Ti if

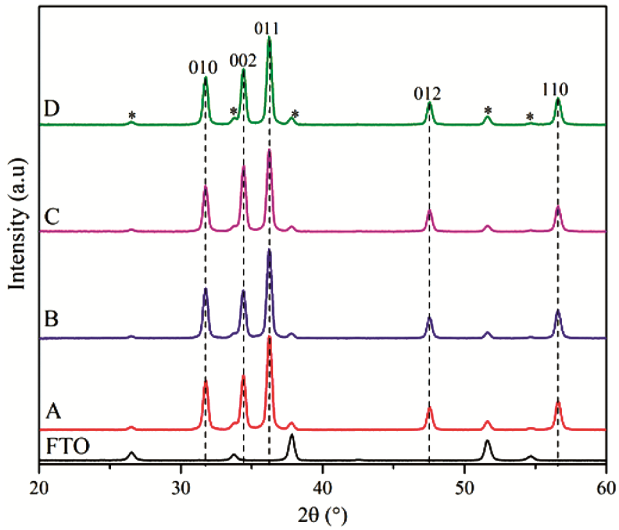

Fig. 4 — XRD pattern of samples (a) ZnO, (b) ZnOTi 0.02 M, (c) ZnOTi 0.04 M and (d) ZnOTi 0.06 M.

Table 2 — FWHM values and crystal size of pure ZnO and ZnO doped Ti

Sampel	FWHM	D (nm)
ZnO	0.28	32.24
ZnO : Ti 0.02 M	0.33	27.64
ZnO : Ti 0.04 M	0.29	31.46
ZnO : Ti 0.06 M	0.43	21.49

compared to pure ZnO. Which is implied that the relaxation of the lattice due to the substitution of Zn^{2+} which has ionic radius 0.74 *Å* which more bigger than ionic radius of Ti^{4+} 0.68 *Å*[13].

3.3 FESEM-EDX Analysis

The morphological properties from pure ZnO and ZnO doped Ti were investigated using FESEM which are represented in the Fig. 6. From those Figure, it can be clearly seen that ZnO has been successfully grown on the FTO substrate. It can be investigated that the grown pure ZnO and ZnO doped Ti has nanorods morphology. In accordance with the results of XRD analysis that crystal structure form samples has hexagonal cross-section. It can be observed that nanorods ZnO are formed with different diameter size. The Ti substituted into ZnO lattice affects structure and size of nanorods ZnO.

Table 3 — The shifted diffraction peak value

Sample	2θ
ZnO	36.19
ZnO: Ti 0.02 M	36.23
ZnO : Ti 0.04 M	36.23
ZnO : Ti 0.06 M	36.24

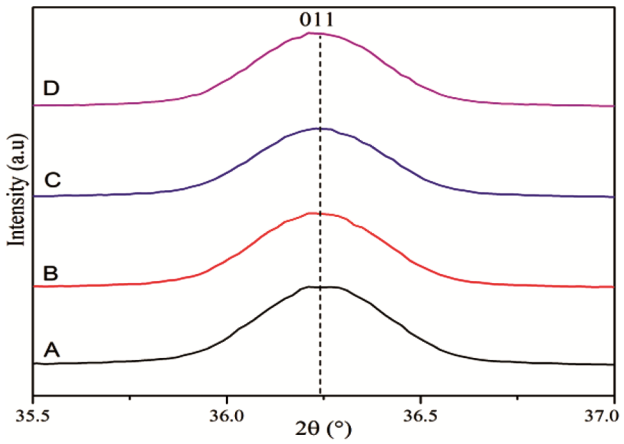

Fig. 5 — The diffraction shifted in orientation plane (011).

Based on FESEM analysis more increased Ti concentration, nanorods ZnO more bigger. ZnO nanorods have less than perfect and uneven shape. That is due to the effect of high concentration of doping solution makes formed nanorods ZnO thicker because of Zn^{2+} ion diffuse faster when concentration of doping solution increases[19].

Figure 7 shows cross-section photos showing the thickness of nanorods ZnO formed each variation of Ti concentration. It can observed that the thickness increases with increasing Ti concentration.

EDX analysis can be seen in Fig. 8 (a) and (b). It is noticed that the element contained in the sample consist of carbon (C), oxygen (O), zinc (Zn) and tin (Sn) all the details are seen in the Figure. The element of C is due to a contamination from samples attached to seeding or growing process. The presence of element C comes from the chamber where the sample is attached. The presence of an element O is part of the oxide layer[20]. In the Fig. 8(b) there is undetectable element of Ti atom. This is because of the photon energy Lα of Ti element (0.45 KeV) which is overlaps with Kα from O element (0.52 KeV)[20]. The high percentage of weight by element O becomes dominant in the EDX spectrum when it compared to Ti.

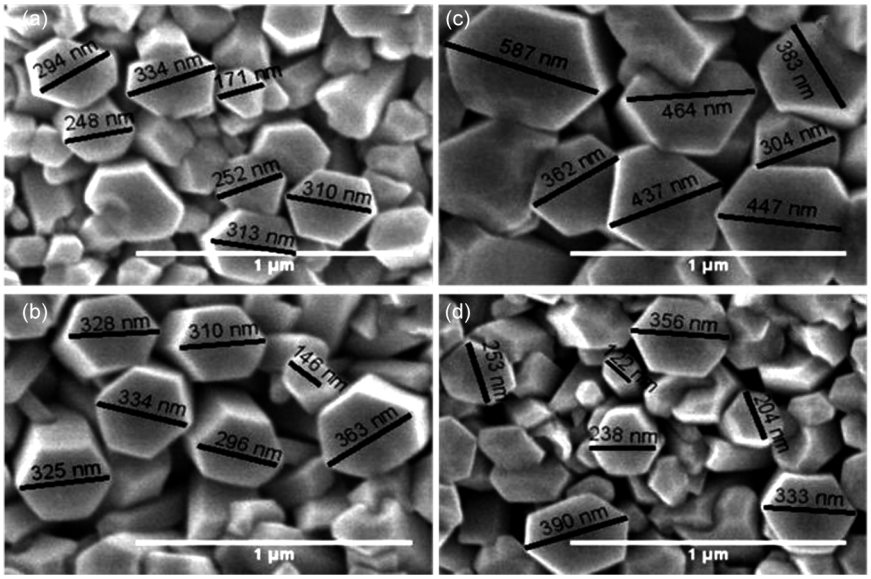

Fig. 6 — FESEM images from nanorods (a) ZnO, (b) ZnO doped Ti 0.02 M, (c) ZnO doped Ti 0.04 M and (d) ZnO doped Ti 0.06 M.

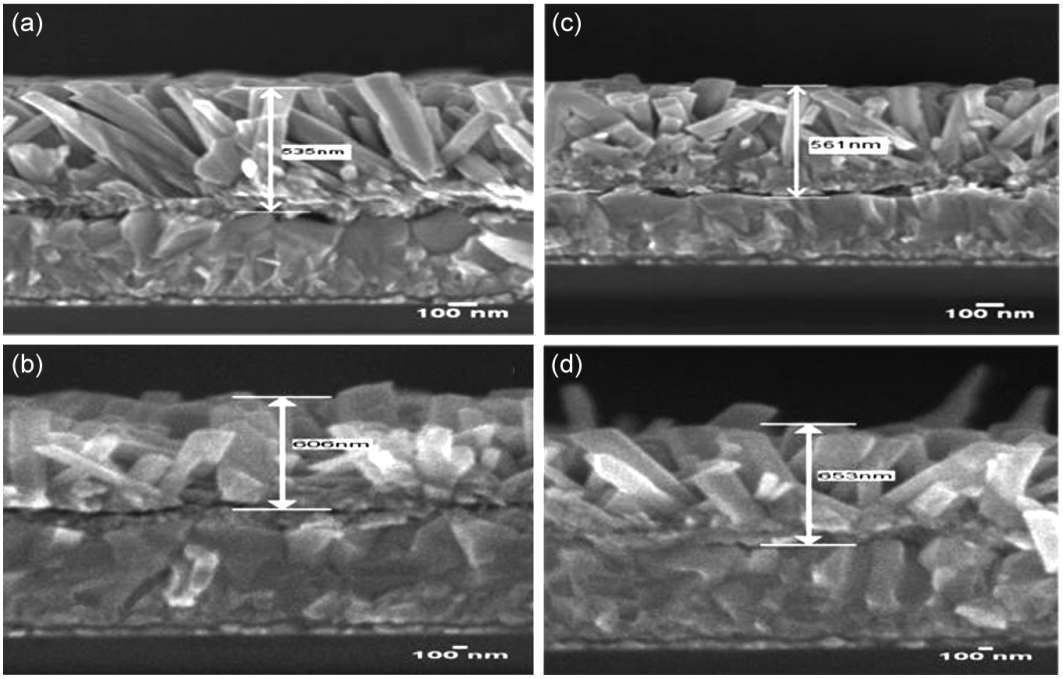

Fig. 7 — Cross-sectional images by FESEM from nanorod (a) ZnO, (b) ZnO:Ti0.02 M, (c) ZnO:Ti0.04 M and (d) ZnO:Ti0.06 M.

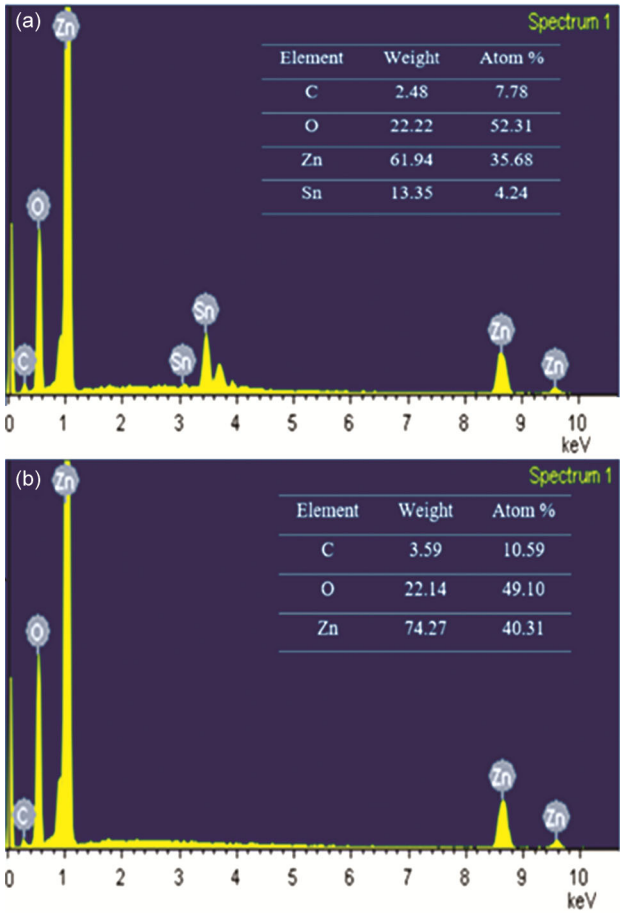

Fig. 8 — EDX analysis from samples (a) ZnO and (b) ZnO:Ti0.02 M.

Table 4 — The results DSSC based on nanorodZnO performance measurement with vary Ti concentration

Sample	Jsc (mA/cm^2)	Voc (V)	FF (%)	PCE (%)
ZnO	4.11	0.41	34.14	0.58
ZnO:Ti (0.02 M)	5.52	0.42	41.94	0.98
ZnO:Ti (0.04 M)	12.85	0.50	33.75	2.19
ZnO:Ti (0.06 M)	6.57	0.41	39.95	1.09

3.4 Photovoltaic (PV) Performance of DSSC

The effect of Ti doping on DSSC efficiency was analyzed using J-V characteristics under halogen lamps with an intensity of 100 mW/cm^2. The performance of DSSC based on ZnO doped with Ti has been summarized in Table 4 and for J-V characteristic are shown in Fig. 9. Ti doping causes an increase in the Jsc. This increase occurs due to the electron transfer processes. Electron that injected to photoanode are easily moved to anode. It is because of the differences between energy labels and charge separation[3]. Based on Fig. 9, Ti concentration 0.04 M shows the largest area if compared to others.The increased of Jsc and Voc can be attributed to enhance light harvesting efficiency in photoanode[13]. We can assumed that this sample absorbs much photon and generates the highest number of electron-hole pairs[21] and it can be seen based on the results of the characterization that has been analyzed. The enhancement of DSSC performance related to the increasing of photoactivity properties and facile carrier transportation in the device[22].

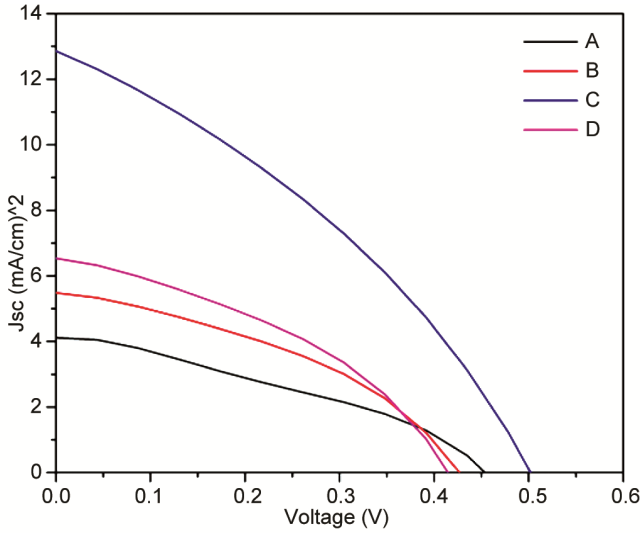

Fig. 9 — J-V curved of DSSC based on nanorod (a) ZnO, (b) ZnO:Ti0.02 M, (c) ZnO:Ti0.04 M and (d) ZnO:Ti0.06 M.

4 Conclusions

Effect of ZnO doped with vary concentration of Ti has been carried out and it is significantly modified the optical, structural and morpohological properties of ZnO. It can be improved optical density, band gap energy and surface area. Based on this results Ti can enhance the efficiency of DSSC which is increase from 0.58 for pure ZnO to 2.19 for ZnOTi0.04 M. The present of Ti should be potential used for photoactivity improvement for DSSC

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