The simple fabrication of nanorods mass production for the dye-sensitized solar cell

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Abstract. ZnO nanorods were successfully synthesized by the plasma torch with the zinc powder as the source of ZnO. Several testing was conducted to examine the results of ZnO nanoparticles among others are X-ray fluorescence (XRF), Scanning Electron Microscopy (SEM), and X-ray diffraction (XRD). The results of ZnO nanorods diameter vary from 87 nm to 263 nm which can be seen from SEM images and it is length varies from 300 to 1000 nm. It was found from XRD data that a sharp peak occurred at 36.253° . It is indicated a good crystal growth and agreed well with the standard data (JCPDF-ICDD card no.: 36-1451). Effects of electrical current variations of plasma torch of 20, 25, and 30 Amperes on the size of ZnO nanorods are indicated from aspect ratio (72.85, 87.42, and 103 nm). The effects of electrical current of plasma torch on the purity of ZnO were about 95.61%, 98.46%, and 96.49% respectively. The performance of the solar cell at the time with the values of Voc, Jsc, FF, and efficiency are 0.466 V, 1.524 mA/cm², 51.95%, and 0.37% respectively. ZnO nanorods were successfully synthesized by the plasma torch with the zinc powder as the source of ZnO.

1 Introduction

Dye sensitized solar cells (DSSC) is one application of energy harvesters with low operational cost. Zinc oxide with a similar band gap and comparable electron injection process to that of TiO₂, has been proven to be one of the most promising alternatives photoelectrode materials for application in DSSC. Compared to ZnO or TiO₂ nanoparticle films, single crystals of these materials exhibit significantly faster electron transport and greater electron mobility. The faster electron transport is a result of the high electron diffusion coefficients, which will provide significant advantages to device performance [1,2].

The greater electron mobility is due to the direction and uninterrupted conduction channel, which can improve the efficiency of charge collection and enable the production of optically thick cells which absorb more incident light [3,4]. In spite of the improved charge transport and the larger electron mobility, one-dimensional (1D) ZnO nanowires show a smaller total surface area for nanowire arrays, as compared to the best TiO₂ nanoparticle devices, which adsorb less dye per unit thickness of the cell and thus absorb less light and collect less charge. As a result, the energy conversion efficiency of ZnO nanowire-based DSSC is typically lower [1,5].

To encourage the application of solar cells in real time, various studies have been directed to look for ways to improve the performance of solar cells DSSC. Strategies for reaching the larger currents from solar cells

is to simplify and streamline the movement of electrons which of them is to use a semi-conductor single crystalline nanowires, nanofibers, arrays of nanotubes, and core-shell structure [6].

Due to their diverse application in optical, electrical, optoelectronic, photo catalytic, hydrophilic, hydrophobic, pigments, metal compounds, medical ointments and cosmetics, nanometric ZnO such as nanospheres, nanoplates, nanosheets, nanoboxes, nanomallets, nanotripods, nanobelts, nanosprings, nanorings, nanocages, nanoneedles, nanorods, nanotubes, nanopropellers, nanoflowers and nanowindmills have been the attractive research topics in nano science and technology for few decades [7-18].

Various ZnO nanostructures have been extensively investigated for DSSC. In the early reports on ZnO-based DSSC, ZnO nanoparticles were often used as the photoanode prepared by a conventional doctor blade technique [56]. The experimental results of a new solar cell fabricated from an electron-accepting layer of freestanding ZnO nanowires [57]. The nanowire DSSC is an exciting variety of the most successful of the excitonic photovoltaic devices [58]. As an ordered topology that increases the rate of electron transport, a nanowire electrode may provide a means to improve the quantum efficiency of DSSC in the red region of the spectrum, where their performance is currently limited. Raising the efficiency of the nanowire cell to a competitive level depends on achieving higher dye loadings through an increase in surface area [59].

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Recently, various techniques have been proposed for ZnO nanoparticles fabrication. It can be classified into either physical or chemical methods [19,20] such as thermal hydrolysis [21], hydrothermal processing [22], sol-gel [23-24], vapor condensation [25], spray pyrolysis [26-27], pulse laser decomposition [28], laser ablation [29], thermal evaporation [30,31], pulse combustion – spray pyrolysis [32], electro-mechanical [33], flame spray pyrolysis [34], direct precipitation [35] and thermal plasma [36,37,38]. More specific, the synthesis of ZnO nanorods has also been performed using various techniques such as hybrid wet chemical route [39], solution process at low temperature [40], physical evaporation [41-43], electrophoretic deposition [44], radio frequency (RF) magnetron sputtering [45], templating against anodic alumina membrane [46] and PTFE capillary tube reaction [47]. Nonetheless, it is important to note that the efficiency and size control still become major research problems in synthesizing ZnO nanoparticles [38].

2 Methodology

ZnO nanorods were successfully synthesized by the plasma torch reactor, as shown in Fig.1 which was operated at atmospheric pressure and less than 3 KW input plasma power. It can be seen that the reactor composed of five main parts among others is a feeder screw as zinc feeder, a plasma torch reactor as main reaction place, a DC plasma as a plasma power source, a filter and a suction blower. Commercial zinc powders from MERCK made in Germany. It has an average particle size of about 45 μ m was employed in this study. The impurity of raw material has been checked using X-Ray Fluorescence (XRF– PANalytical-Minipal QC) giving results of 98.9% purity of zinc and containing impurities such as Ca, Cr, Fe, and Ni.

A screw conveyor fed zinc powder into the plasma torch reactor at the fix rate of 2 g/min with gas carrier. These having entered the plasma torch reactor then faced plasma zone, then vaporization and oxidation were experienced by the zinc powders immediately forming ZnO nanoparticles.

The time elapsed to form ZnO nanoparticles under this process take about 0.01 s [36]. The results of vapors from burning process were then dropped to silo, then sucked by blower passed through the filter tube so that ZnO powders could be seized by filter membrane. Electrical currents inputted to the plasma poles (cathode and anode) were varied from 20, 25, and 30 Ampere .

Several testing was conducted to examine the results of ZnO nanoparticles among others, are X-ray fluorescence (XRF-PANalytical-Minipal QC), X-ray diffraction (XRD-PHILLIP-XPRT PRO) and Scanning Electron Microscopy (SEM-FEI-Inspect S50), To ensure the purity of synthesized rod-like ZnO nanoparticles, XRF (PANalytical-Minipal QC) operated at 20 kV was used as qualitative and quantitative elemental analysis.

NO	DESCRIPTION	MATERIAL
1	WATER INLET	SUS304
2	WATER INLET	SUS304
3	PLASMA OUTPUT	
4	WATER OUTLET	SUS304
5	BOTTOM GRAPHITE	GRAPHITE
6	COMPRESSION AIR	SUS304
7	WATER OUTLET	SUS304
8	TOP GRAPHITE	GRAPHITE
9	COMPRESSION AIR INLET	SUS304
10	ZINC POWDER INLET	SUS304
11	FEEDER SCREW	SUS304
12	STEPPER MOTOR	
13	ZINC POWDER SILO	SUS304

Fig. 1. The Simple Plasma Torch Machine Design.

In case of crystallite size and phase identification, an examination of the as-prepared ZnO nanorods involved X-ray diffraction analysis by the 2- θ method. XRD (PHILLIP-XPRT PRO) was equipped with Cu Ka ($\lambda=0.154060$ nm) radiation at 40 kV and 30 mA. For each step, the scanning step size and collection time were set at 0.02 and 0.5 respectively.

Scanning electron microscopy (FEI-Inspect S50) operated at 20 kV was used to capture the morphology of the synthesized ZnO nanorods.

The DSSC consisted of a conducting glass, the ZnO, dye-absorbing electrode, the electrolyte, and a counter-electrode layer. The fluorine-doped tin oxide (FTO), used as the conducting glass substrate, was prepared using spray pyrolysis [50]. A solution of tin (II) chloride dihydrate (16.12 g, $\text{Cl}_2\text{Sn} \cdot 2\text{H}_2\text{O}$, Merck), ammonium fluoride (0.265 g, NH_4F , Merck), and ethyl alcohol (100 ml, 96%, Merck) of 100 ml was mixed and sprayed on the glass surface, followed by heating at 450°C [55]. 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_2PtCl_6 solution (Merck) onto the FTO glass, followed by heating at 300°C and subsequent cooling [51].

The fabrication of the nanorods ZnO working electrode, a homogenous paste containing nanorods ZnO semiconductor (0.5 g) and ethyl alcohol (0.4 mL, 96%, Merck) was prepared. The paste was then cast onto the FTO glass ($1\text{cm} \times 3\text{ cm}$) using the doctor-blade method. For a strong bonding between the ZnO film nanorods and the FTO glass [52, 53], the ZnO paste-coated FTO glass was sintered at 450°C for 2 h and subsequently cooled. Afterwards, the ZnO working electrodes were immersed in the respective dye solutions for 24 h at room temperature, prior to the DSSC assembly [53, 54].

The electrolyte solutions for the DSSC were prepared as follows: sodium iodide (3.3 g, 99.9%, Merck) and acetonitrile (30 ml) were dissolved by stirring for 20 minutes, prior to adding iodine (524 g, 99.9%, Merck). The stirring was continued for 24 h to Achieve a homogeneous solution. The electrolyte solution was injected into the assembled DSSC spaced at $50\text{-}\mu\text{m}$ intervals and then sealed. [55]

In this research will be testing the IV characterization tests on solar cells DSSC. The testing uses Xenon lamps under illumination by a lamp of 1000 W/m^2 and solar cell characterization test equipment. For characterization testing of solar cells DSSC several parameters such as J_{sc} Short Circuit Current, Open Circuit Voltage- V_{oc} , and Fill Factor-FF and Efficiency of solar cell DSSC (η) will be tested. This efficiency value which becomes the main reference in determining the quality of performance of a solar cell.

3 Results and Discussion

The diameter of the results of ZnO nanorods varies from 87 nm to 263 nm which can be seen from SEM images with length varies from 300 nm to 1000 nm. Fig.2, Fig.3, Fig.4 shows the morphology and size of the ZnO nanorods. The size of ZnO nanorod range 72 nm - 103 nm. Effects of electrical current variations of plasma torch of 20, 25, and 30 Ampere to the size of ZnO nanorods are also indicated from the aspect ratio of about 72.85, 87.42, and 103 nm.

Table 1 shows the other effects of electrical current variations of plasma torch to the purity of ZnO about 95.61%, 98.46%, and 96.49% respectively.

Table 1. Compound effects of electrical current variations of plasma torch of 20, 25, and 30 Amperes to the purity of ZnO

Ampere	Compound (%)				
	ZnO	CaO	Cr_2O_3	Fe_2O_3	NiO
20	95.61	0.24	0.11	0.15	0.082
25	98.46	0.14	0.098	0.16	0.086
30	96.49	0.55	0.13	0.19	0.13

Fig. 2. Photo of SEM ZnO are formed from zinc powder with the 20 ampere plasma torch process.

Fig. 3. Photo of SEM ZnO are formed from zinc powder with the 25 ampere plasma torch process.

Fig. 4. Photo of SEM ZnO are formed from zinc powder with the 30 ampere plasma torch process

The XRD pattern of resulted ZnO nanorods is performed in Fig.5. In this study, each crystalline structure of ZnO nanorods is a perfect crystal with the growth direction of *c* axis. Three XRD patterns are indexed as hexagonal wurtzite structure of ZnO having space group of P6₃mc (186) with lattice constant sets of *a*,*b*=3.24982 Å and *c*= 5.20661 Å, which is consistent with the values in the database of JCPDF-ICDD card no.: 36-1451 [49]. Nine peaks appear at 2 θ = 31.768°, 34.421°, 36.253°, 47.539°, 56.594°, 62.856°, 66.375°, 67.947°, 69.085°, respective to miller indices of (100), (002), (101), (102), (110), (103), (200), (112), and (201).

Fig. 5. XRD patterns of ZnO nanorods

Moreover, the strong and narrow intensity diffraction peaks imply the good crystalline nature and size of the synthesized products. Average nano-crystalline sizes (*D*) obtained from the broadening of XRD peaks are calculated using Scherer's formula as follows [9]:

$$D = \frac{0.94 \lambda}{B \cdot \cos \theta} \quad (1)$$

Where *D* is the crystal size, *B* is the broadening from the sample or its full width half medium (FWHM), λ is the wave length of X-ray, θ is the Bragg's angle. Calculation results using Equation (1) are listed in Table II.

Table 2. FWHM and crystalline size of ZnO nanorods.

Miller index	2 theta (deg)	FWHM	Crystalline size (nm)
(100)	31.768	0.227	31.7406
(002)	34.421	0.191	37.9835
(101)	36.253	0.226	32.2650

The XRD data shows a sharp peak at 36.253° which indicates a good crystal growth and agrees well with the standard data (JCPDF-ICDD card no.: 36-1451) [49].

Fig. 6. *J*- *V* curves of ZnO nanorods

In Fig.6, it has shown the performance of the solar cell at the time with the values of *V*_{oc}, *J*_{sc}, FF, and efficiency generated are respectively 0.466 V, 1.524 mA/cm², 51.95%, and 0.37%.

4 Conclusion

ZnO nanorods were successfully synthesized by the plasma torch with the zinc powder as the source of ZnO. ZnO nanorods have a high purity ZnO composition. The plasma torch is a simple fabrication of ZnO nanorods mass production of dye sensitized solar cell. The advantages of this method are simplicity and potential use for future large scale preparation of ZnO nanorods, which is useful for many source of energy applications.

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