

FABRICATION OF DYE-SENSITIZED SOLAR CELL BASED ON ZINC OXIDE NANORODS

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Abstract

Zinc oxide nanorod with hexagonal structure was achieved by using chemical bath deposition method under atmospheric pressure by using zinc nitrate hexahydrate [Zn(NO₃)₂.6H₂O] and hexamethylene-tetramine (C₆H₁₂N₄) at constant temperature 93°C and the deposition time of 2 hours, 4 hours and 6 hours. The prepared film was grown on the surface of zinc oxide seed layer. The surface morphologies and the structural characterization of zinc oxide (ZnO) nanorods were characterized by Scanning Electron Microscope (SEM) and X-ray Diffraction (XRD) technique. The XRD pattern of the sample revealed that ZnO nanorods have hexagonal crystallite structure. Photovoltaic parameters such as short circuit current density J_{sc} , open circuit voltage V_{oc} , fill factor FF, and overall conversion efficiency η for the fabricated cells were determined under illumination. In the analysis of photoelectrochemical properties, ZnO DSSC showed more pronounce in their performance and it has the efficiency of 0.12%.

Keywords: Dye-sensitized solar cell, Zinc Oxide nanorod, seed layer

Introduction

Zinc oxide (ZnO) is an important material and has received considerable attention due to its applications in electrical, optical, mechanical and scientific research as well as industry (Xia Y *et al*, 2003). Zinc Oxide is a wide band gap (3.37 eV) semiconductor and has a large binding energy (60 MeV), low resistivity and high transparency in the visible range and high light trapping characteristics (Lee GJ *et al*, 2010). It has also attracted attention for electrical and optical applications such as light-emitting diodes, photocatalysts, photodetectors, piezoelectronic devices, sensors and solar cells (Samanta P *et al*, 2009). ZnO has some benefits since it is cheaper, its band gap is wide so it is easily grown up on the substrate, it is non-toxic and environmentally friendly. Conventional solar cells are based on light harvesting and charge separation at semiconductor p-n junctions the technology used to produce energy from the solar radiation. The technological development in novel approaches exploiting thin films, organic semiconductors, and dye sensitization (Park WI *et al*, 2005). Nanostructured ZnO has been synthesized via a wide range of techniques (Hossain M *et al*, 2005). Among these methods, the chemical bath deposition method has drawn a considerable amount of attention in scientific and technological fields because of its considerable advantages of generally low temperature processing conditions, easy composition control and homogeneous easy fabrication of thin films with large area and low cost (Gowthaman *et al*, 2011). Here in, synthesis of ZnO nanorod (NRs) that have been carried out were such as chemical bath deposition (CBD) method at low temperature.

Nanostructures and surface morphologies of ZnO NRs were investigated by X-ray diffraction (XRD), and Scanning Electron Microscope (SEM). Photovoltaic properties of the ZnO NRs solar cells were investigated by measuring current density-voltage characteristics and

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incident photon to current conversion efficiency. The highest conversion efficiency was obtained in ZnO NRs with the longest deposition time.

Experimental Details

2.1 Materials

Analytical grade (BDH, England) Zinc Acetate Dihydrate ($\text{ZnC}_4\text{H}_6\text{O}_4$), Zinc Nitrate Hexahydrate [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$], Hexamethylenetetramine ($\text{C}_6\text{H}_{12}\text{N}_4$), Sodium Hydroxide (NaOH), Isopropanol Alcohol ($\text{C}_3\text{H}_8\text{O}$), distilled water (H_2O) and deionized water (DI) were used as starting precursor. All chemicals were used as purchased without further purification.

2.2 Cleaning Procedure of Glass Substrate

The very first step before the CBD proper is the washing of glass substrate in order to remove dirt and impurities that may have unknowingly settled on the glass substrate. This is done by washing in several substances, namely: acetone, distilled water, ethanol, distilled water again, hydrochloric acid (HCl) and lastly distilled water. These glass substrates are then dried in air blow at room temperature.

2.3 Seeding Method and Chemical Bath Deposition (CBD) Method

The seeding method commence with the making of zinc acetate dihydrate [$\text{Zn}(\text{OOCCH}_3)_2 \cdot 2\text{H}_2\text{O}$] (0.02M) was ground for 15 min and then mixed with 0.02 M of NaOH. After the mixture was ground for 2 hr, the product paste was washed many times with deionized water. The resultant paste was centrifuged for 30 min to obtain pure ZnO precipitation. This paste was mixed with isopropanol alcohol [$\text{C}_3\text{H}_8\text{O}$] (10ml) to get the ZnO seed solution. This solution was coated on glass substrates by rod coating method. The thickness of the zinc acetate layer can be controlled by the number of rod coating runs and show good reproducibility. The coated substrates were dried at room temperature and annealed at 350°C for 30 min. All the substrates were seeded before the final growth of zinc oxide (ZnO) nanorods.

For chemical bath deposition (CBD) growth process, the aqueous solution of zinc nitrate hexahydrate [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$], and hexamethylenetetramine ($\text{C}_6\text{H}_{12}\text{N}_4$) were first prepared. The concentrations of both were fixed at 0.1M. The aqueous solutions of zinc nitrate hexahydrate [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] (100 mL) and hexamethylenetetramine ($\text{C}_6\text{H}_{12}\text{N}_4$) (100 mL) were mixed together in 250 mL beaker. The bath is stirred at a constant rate of 360 RPM by magnetic stirrer for 30 minutes at room temperature. The beakers containing the bath solutions and the substrates were put on the hot plate for 2 hours, 4 hours and 6 hours at a constant temperature of 93°C . After the growth, the substrates were removed from the solutions, rinsed with acetone, distilled water, ethanol then acetone and dried at room temperature. A post growth annealing was performed for the substrates (samples) at 550°C for 1 hour and then quenched to room temperature (Li Z *et al*, 2008).

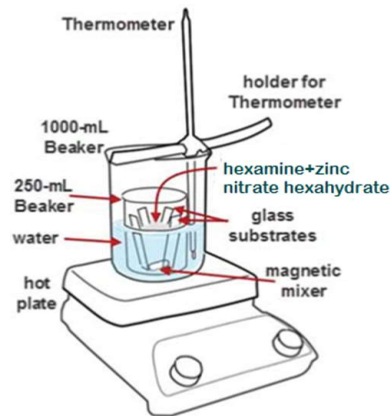


Figure 2 The schematic diagram of chemical bath deposition of ZnO nanostructure

2.4 Dye-Sensitized Solar Cells

The typical structure of DSSCs based on ZnO nanorod is shown in Figure 2.2. A few micrometer-thick layer ZnO nanorods is deposited on one of the electrodes and it acts as a photoanode in DSSCs. Dye molecules (erosin Y) are attached onto the surface of the photoanode and an iodine electrolyte is filled between the two electrodes. On the other electrode, a thin layer of graphite is generally deposited for high catalytic activity.

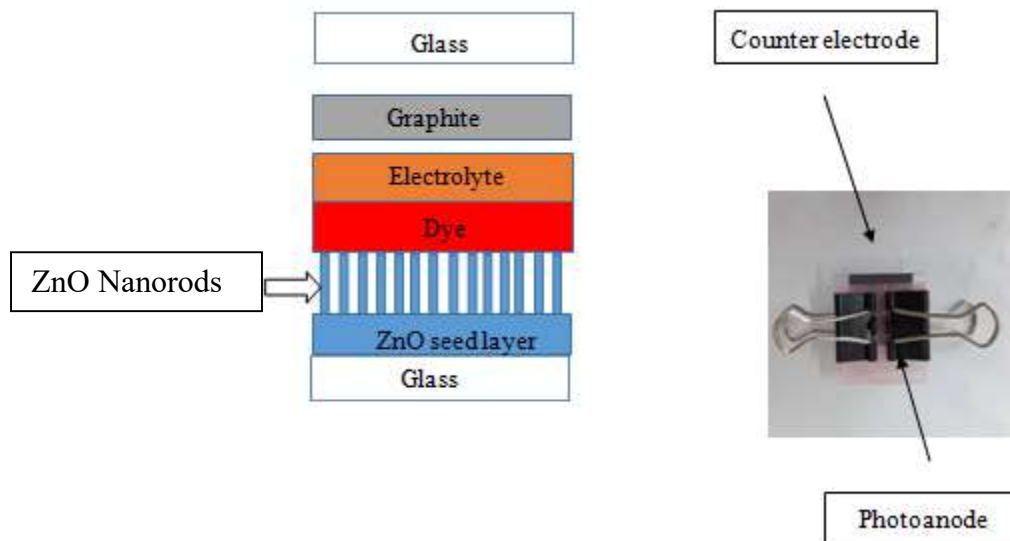


Figure 2.2 The typical structure of DSSCs based on ZnO nanorods

2.4 Characterization

ZnO nanostructures were confirmed by X-ray powder diffractometer (XRD) (Type: RIGAKU-RINT 2000) and Scanning Electron Microscope (SEM) (Type: JEOL 15 kV).

Results and Discussions

3.1. SEM and XRD Analysis for CBD

To compare ZnO nanostructures grown on different deposition time, SEM images of ZnO nanostructures on the seed layer were performed, as shown in Figure 2.

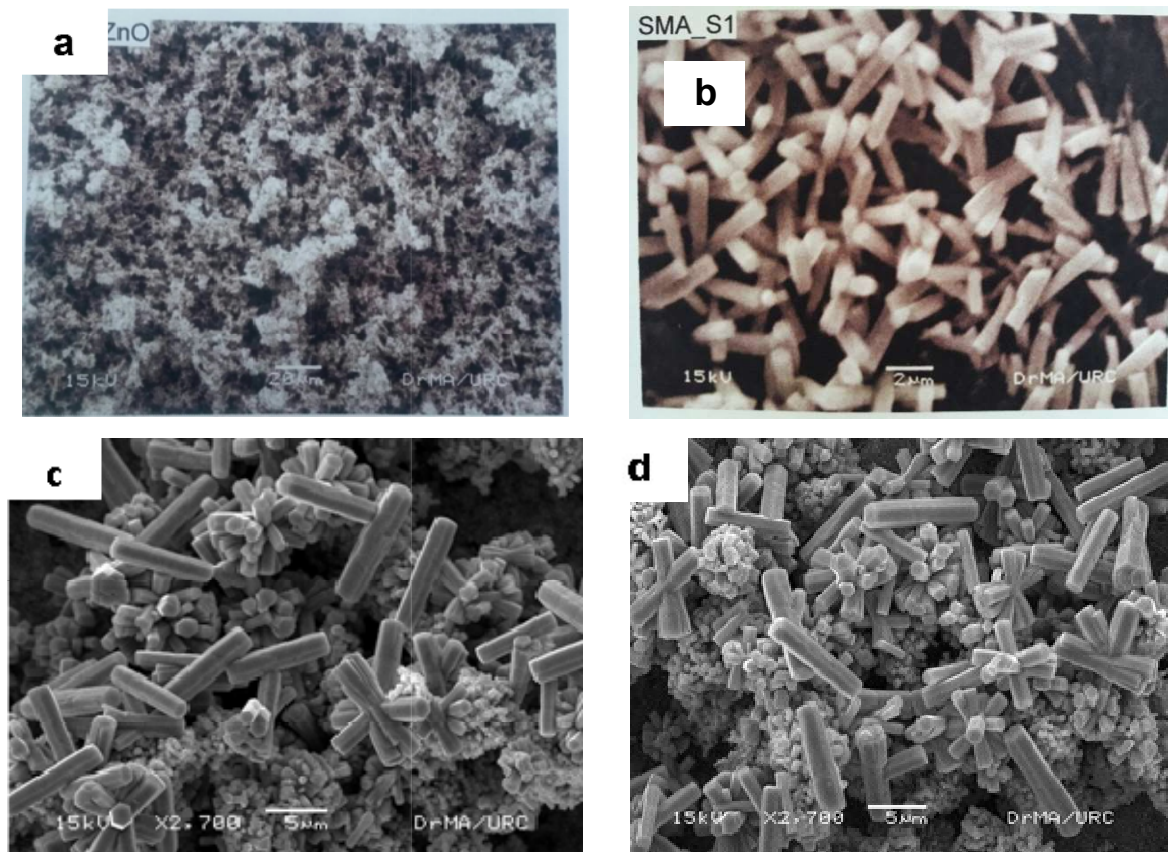


Figure 2 Top-view SEM images of ZnO samples (a) ZnO seed layer which is coated on the glass substrate (b) ZnO nanorod which is grown on seed layer for two hours deposition time (c) four hours deposition time (d) six hours deposition time

The SEM results reveal that the formation of nanorods and nanoflowers are formed in these samples. Figure 2(a) shows the ZnO seed layer and the particle size of the ZnO is approximately 100 nm. A thin layer of densely and uniformly dispersed ZnO nanoparticles is used as a seed layer for chemical bath deposition. It is noteworthy that the variation in the deposition time leads to a significant change in the growth of the ZnO NRs. When two hour deposition time, the nanorod structure is achieved. When the deposition time is increased, the size of the nanorod is bigger and become the flower like nanostructure. During the growth process, the tips of several NRs touch and/or cross each other, initially because of their slightly tilted growth and the piezoelectric properties of ZnO NRs, which lead to an increase in the diameter of the NRs and forming the flower like structure with an increase in the deposition time. The SEM characterizations of the as-synthesized zinc oxide (ZnO) nanoflowers are shown in Figure 2 (c) and (d). SEM micrographs show that the lengths of zinc oxide (ZnO) nanoflowers are more than 2 μm in diameter from 0.476 μm to 0.756 μm .

The XRD results of different deposition time give similar pattern. The XRD analysis of ZnO NRs phase informed that the formed diffraction pattern was in accordance with the data of XRD JCPDF standard No.89-1397 with the hexagonal crystal (zincite) system having the space group of P63mc, with the crystal lattice of $a, b = 3.2533 \text{ \AA}$ and $c = 5.2073 \text{ \AA}$. The formed phase was suitable for the report of Rai, et al, that ZnO NRs were formed in zincite phase. Figure shows the diffraction peak located at (100), (002), and (101). The XRD pattern with the annealing temperature of $550 \text{ }^\circ\text{C}$ for one hours at the NRs growing temperature of $93 \text{ }^\circ\text{C}$ had the crystal orientation at the highest intensity peak on (101), while on (100) and (002) the pattern weakened orientation. The XRD pattern exhibited that of the (ZnO) nanoflowers had good crystal quality. Diffraction peaks related to the impurities are not observed in the XRD pattern, confirming the high purity of the synthesized NRs.

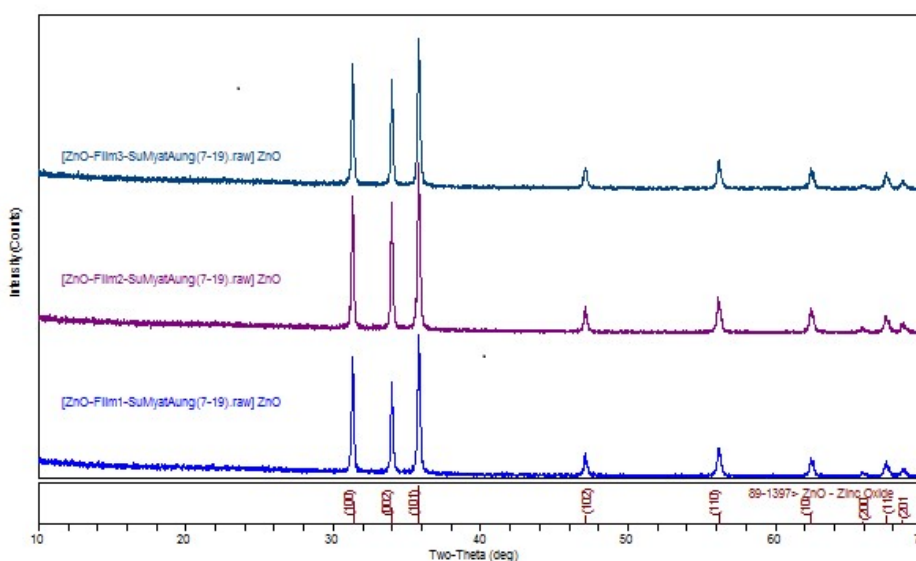


Figure 3 shows the XRD results of ZnO Seed layer and ZnO NRs with the precursor concentration of the various growing times of 2 hours, 4 hours and 6 hours.

Figure 4 shows the current-voltage I-V characteristics for DSSCs constructed using nanorod and nanoflower films measured under a simulated illumination with a light intensity of 11 mW/cm^2 . The short-circuit current (J_{sc}) open-circuit voltage (V_{oc}), FF and PCE derived from the I-V curves under illumination for both nanorod and nanoflower based DSSCs are also presented in the inset table 1. From Figure. 3, it can be seen that the J_{sc} , V_{oc} , and FF for the cell constructed using nanoflower film (6 h deposition time) $I_{sc} = 78 \text{ } \mu\text{A/cm}^2$, $V_{oc} = 0.5V$ and $FF = 0.11$ represent clear improvement over the cell constructed using nanorod array (2 h deposition time) $I_{sc} = 37.1 \text{ mA/cm}^2$, $V_{oc} = 0.3V$, and $FF = 0.03$. Due to much improved I_{sc} and FF, the nanoflower based cell reached a total power conversion efficiency of 0.12%, outperforming that of the nanorod-based cell 0.033%.

Table 1 Photovoltaic parameters of DSSC solar cell based on ZnO nanorods with various growing times

	I_{sc} (μA)	V_{oc} (mV)	I_m (μA)	V_m (mV)	FF	η (%)
ZnO 2 hr deposition	37.1	295	20	200	0.03	0.033
ZnO 4 hr deposition	57	369	30	230	0.06	0.07
ZnO 6 hr deposition	78	480	40	320	0.11	0.12

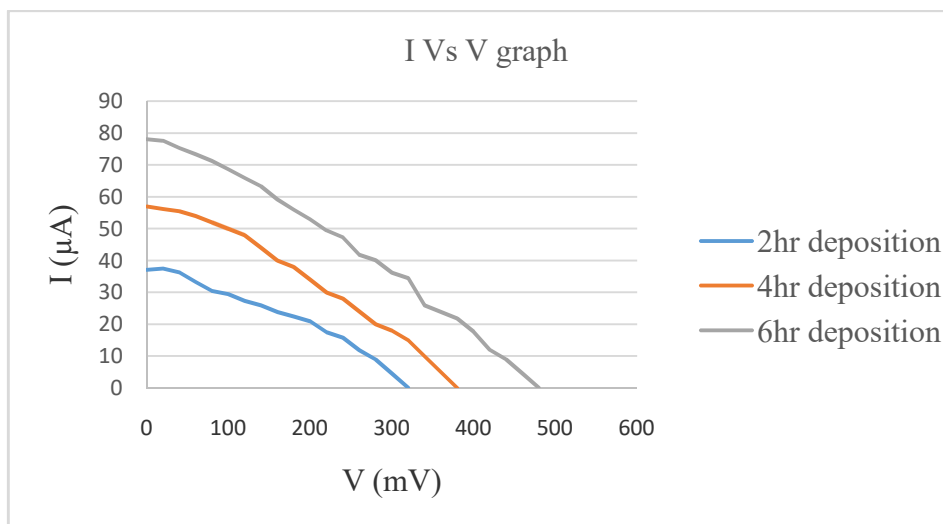


Figure 4 shows the I Vs V graph for DSSC solar cell based on ZnO nanostructure photoanode

Conclusions

In conclusion, Zinc oxide (ZnO) nanorods were synthesized by a chemical bath deposition (CBD) method with wide range of size and various shapes. The XRD analysis shows the ZnO films were hexagonal system structure with (101) oriented planes. The average crystallite size of ZnO was found to be about 31 nm. Current voltage measurement on fabricated dye-sensitized solar cell using eosin Y dye extract shows the 2 hours deposition for open circuit voltage about 300 millivolts and short circuit current of 40 microamperes, 4 hours deposition for open circuit voltage about 400 millivolts and short circuit current of 60 microamperes and also 6 hours deposition for open circuit voltage about 500 millivolts and short circuit current of 80 microamperes, respectively.

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