Synthesis, structural and optical properties of ZnO Nano-rods used in Solar Cells fabrication

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Abstract- Sudan has vast areas of fertile land, abundance of minerals, water, winds and sunshine, many types of these energies become a valid option. However, in this research, the focus shall only be concerning one type of renewable energy, which is solar energy. The conventional solar cells are mainly made up of doped silicon electrodes. Their major task is to convert visible light to electrical energy according to the photovoltaic (PV) conversion method. However the production of these crystalline silicon solar cells is very complicated and expensive. Therefore the aim of this research is to produce ZnO nano-rods with optimum characteristics that can be used in the construction of low-cost solar cells. Zinc Oxide (ZnO) nano-rods in powder form were synthesized using the hydrothermal method, which is a simple and inexpensive method. The refinement of X-Ray diffraction (XRD) pattern was used to find and investigate the structural properties of the nano-rods. The morphology and size of the ZnO nano-rods were determined by a Transmission Electron Microscope (TEM), while the EDX studies confirmed the formation of ZnO functional group. The optical band gap energy was obtained using both UV-VIS-NIR diffuse reflectance and absortion spectroscopy also photo-luminesces (PL) was used.

Keywords: ZnO nanorods, solar cells, hydrothermal method.

المستخلص – تتكون الخلايا الشمسية التقليدية بشكل رئيسي من أقطاب سليكونية مشوبة. وتتمثل مهمتهم الرئيسية في تحويل الضوء المرئي إلى طاقة كهربائية وفقًا لطريقة التحويل الكهروضوئية (PV). ومع ذلك فإن إنتاج هذه الخلايا الشمسية السليكونية البلورية معقد للغاية ومكلف. ولذلك فإن الهدف من هذا البحث هو إنتاج قضبان أكسيد زنك النانوية لها خصائص مثالية يمكن استخدامها في بناء الخلايا الشمسية منخفضة التكلفة. تم تصنيع قطبان أكسيد الزنك (ZnO) النانوية في شكل مسحوق باستخدام الطريقة المائية الحرارية ، وهي طريقة بسيطة وغير مكلفة. تم استخدام تقنية حيود الأشعة السينية (XRD) للبحث عن الخصائص التركيبية للقضبان النانوية والتحقق منها. تم تحديد مورفولوجيا وحجم قضبان النانوية ZnO بواسطة المجهر الإلكتروني النافذ (TEM) ، في حين أكدت دراسات EDX تشكيل مجموعة وظيفية ZnO. تم الحصول على طاقة الفجوة في النطاق البصري باستخدام مطيافية الانعكاس المنتشر UV–VIS–NIR والتشويش الضوئي (PL) والاستضاءة الضوئية.

INTRODUCTION

There are many types of renewable energy sources which provide clean environmental-friendly energies. Such as biomass (bioenergy), hydropower, solar, wind energies and many others. In a country like Sudan that has vast areas of fertile land, abundance of minerals, water, winds and sunshine, many types of these energies become a valid option. However, in this research, the focus -shall only be concerning one type of renewable energy-that is, the Solar Energy. solar energy as being one important renewable energy so that Sudan needs to turn towards. Sudan has been considered as one of the best countries for exploiting solar energy since its average sunshine duration ranges from 8.5 to 11 hours per day [1].

Most metal oxides and specially ZnO and TiO_2 nanoparticles have been drawing attention for several years due to their semiconducting properties. ZnO has been found to have exceptional and functional properties and are increasingly being considered as inexpensive replacements for silicon in the development of the next generation of solar cells [2]. ZnO nanostructures were found in various morphologies such as nanorods, nanowires and nanotubes, all they have a wide band gap and large exciton binding energy [3]. TiO_2 and ZnO both have high photochemical stability, therefore they were found to be very attractive for solar cell applications [4].

ZnO is an essential material due to its low cost, large band gap, and luminescent properties. Its optoelectronic properties have been studied for photo anodes, short-wavelength lasing, and cathode luminescence because of its broad emission band in the yellow-green region and also for the general nonlinear optical properties of II-VI semiconductors. Lately, ZnO has been used for photovoltaic devices applications [5].

ZnO is known to be a versatile n-type direct wide band gap (3.3 – 3.7eV) semiconductor. It has a large exciton-binding energy of abut ~60 meV at room temperature. Also ZnO has wide-ranging applications in electronic and optoelectronic devices, such as piezoelectric sensors, ultraviolet (UV) blue light-emitting diodes, transistors, field emission displays, gas sensors, UV detectors, transparent conductive films, hybrid solar cells, etc. [4-6].

Dye synthesized solar cells are have proved to be an efficient and inexpensive methods for producing solar photovoltaics compared with the p-n junction semiconductor solar cells, since they depend on dye sensitizers to absorb the visible light and generate an electron transfer reaction [7].The aim of this research is to produce ZnO nano-rods with optimum characteristics that can be used in the construction of low-cost solar cells.

Materials and Method

All chemicals had a purity of 98%, the chemicals that have been used include zinc chloride $ZnCl_2$ (MW 136.286 g.mol-1), sodium hydroxide NaOH (MW 40 g.mol-1) and distilled water. ZnO nanoparticles were synthesized through the hydrothermal method, 20.5 grams of $ZnCl_2$ were dissolved in 500 ml distilled water under stirring, the solution was heated up to 90˚C, then 20 grams of NaOH were dissolved into 50 ml of distilled water and then added drop by drop to $ZnCl_2$ Solution in a period of two hours in order to complete the reaction as shown in equation 1.

$$ZnCl_2 + 2NaOH \rightarrow 2NaCl + Zn(OH)_2 \qquad (1)$$

The resulting solution was washed with distilled water until all salt residuals were removed, then the solution was heated at 850˚C for four hours. After the reaction was complete the ZnO nanorods were heated again in an oven at 300˚C in order to remove any persisting moisture (see equation 2).

$$2Zn(OH)_2 \rightarrow ZnO + H_2 \qquad (2)$$

ZnO nanorod Solar Cell

Conventional solar cells are p-n junction devices are constructed from semiconducting materials. Their function is to convert visible light to electrical energy in agreement with the photovoltaic (PV) conversion method. The most common type of p-n junction solar cells was the crystalline silicon cells that were made up of doped silicon electrodes. Unlike p-n junction solar cells, dye synthesized solar cells (DSSC) depend on dye sensitizers to absorb the visible light and generate an electron transfer reaction [6]. The improvement in construction of DSSCs, has lead to exciting new possibilities for producing solar photovoltaics possibly at lower cost. DSSCs can be very efficient and they were found to have maximum efficiency of ~11% [7].

In this research, ZnO DSSC was fabricated on two types of conductive glass substrates in order to find the optimum properties for the ZnO nanorod DSSC. The ZnO DSSC were constructed by dissolving the ZnO nanorods in powder form in ethanol, then the solution was evenly distributed as layer on the conducting side of heated FTO and ITO substrates. After that Rodhamine B dye was used on the both substrates as a dye sensitizer. The counter electrodes were made of heated substrates covered with iodine. Finally the ZnO DSSCs were exposed to a 0.55(mW/cm2) neon lamp in order find the I-V curve and calculate the fill factor and the efficiency.

Optical Properties

The optical band gap of the ZnO nanoparticles was calculated from the UV data using both absorbance and reflectance spectrums and also from the Photoluminescence (PL) spectrum (see figure . 3). The absorption spectrum of ZnO nanoparticles presented a peak located at ~363 nm as illustrated in Figure. 1, this corresponds to the optical band gap of ZnO that was calculated using Tauc's equation as shown in equation 3 and it was found. to be ~ 3.41. While the optical energy gap of ZnO nanoparticles was calculated form the reflectance spectrum using Kubelka – Munk equation given in term of reflectance (R) as in equation 5. The calculated band gap was found to be ~3.42 . By comparing the two results using different spectrums they were found to be almost equal.

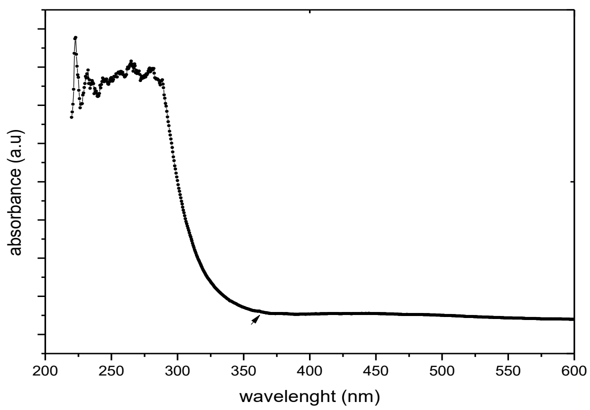

Figure 1: The absorbance spectrum of the ZnO nanorods

$$Eg(eV) = hC/\lambda \approx 1240/\lambda \quad (3)$$

$$R_\infty = \frac{\alpha}{S} = \frac{(1-R_\infty)^2}{2R_\infty} \quad (4)$$

$$F(R_\infty)(h\upsilon)^2 = A((F(h\upsilon - E_g)) \quad (5)$$

Photoluminescence (PL)

Photoluminescence is a procedure in which a molecule absorbs a photon in the visible region, and this leads to the excitation of one of its electrons to a higher electronic excited state, and then a photon is radiated as the electron ascends to a lower energy state. Photoluminescence spectroscopy is a widely used technique for characterisation of the optical and electronic properties of semiconductors and molecules. For the measurement of the luminescence dynamics, Perkin-Elmer (LS-55) luminescence Spectrophotometer was used to determine the emission spectra of the ZnO nanorods powder for different wavelengths as shown in figure. 3.

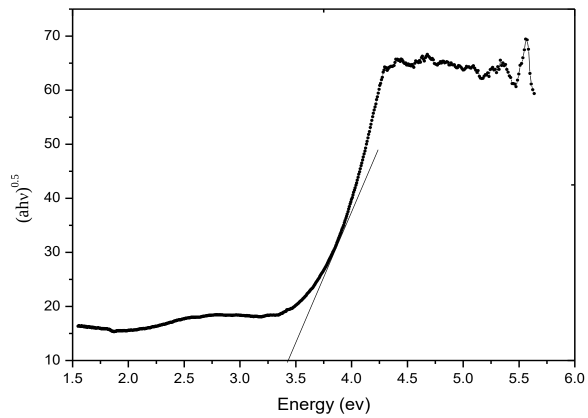

Figure 2: ZnO nanorods Optical band gap from reflectance spectrum

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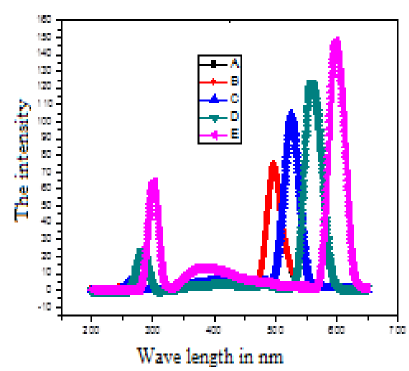

Figure 3 The emission spectra of the ZnO nanorods powder

Structural Properties

The X-Ray Diffraction pattern for the ZnO shown in Figure 4. was characterized by sharp reflection peaks that are an indication to a cubic single phase of ZnO. The atomic and molecular structure of the ZnO structure is clearly preserved throughout the hydrothermal route.

TEM Structure

A transmission electron microscope (TEM) image was used to investigate the morphology and size of the ZnO nanoparticles as shown in Figure 5. The TEM image demonstrated that the particles are nanorods and the length of the rods was found to be in the range from 230 – 292 nm the width of the rods was in the range 49 – 57.3 nm. The difference in nanorod lengthes is due to the slight difference in the growth time for each rod.

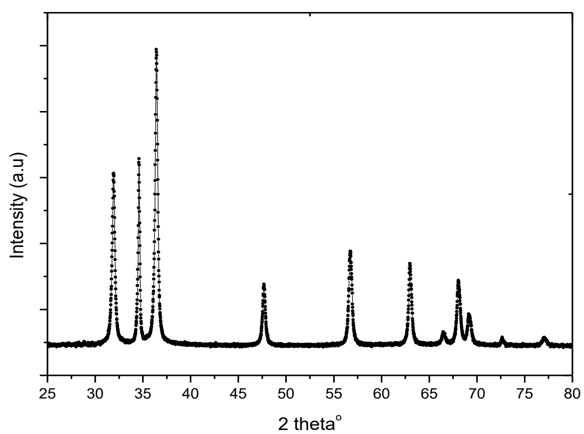

Figure 4: The XRD Pattern of ZnO nanorods synthesized through hydrothermal method.

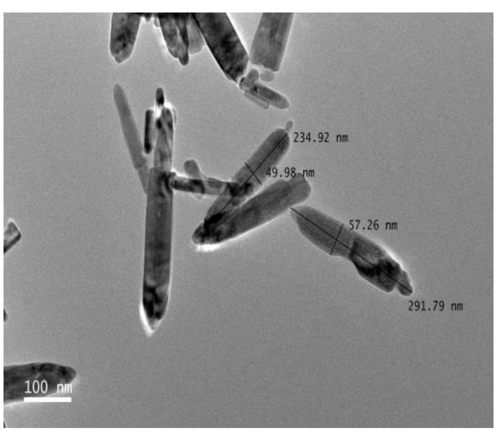

Figure 5: The TEM image of ZnO nanorods

Energy Dispersion X-Ray Fluorescence (EDXRF)

The chemical characterization of the ZnO nanorods was found using an energy dispersive X-ray (EDX) spectroscopy and the results are displayed in Figure 6 and Table1. A conventional Energy-Dispersive X-ray (EDX) analysis of hydrothermal ZnO nanorods was done to verify the atomic composition of the sample, as shown in Figure 5. The ZnO EDX spectra demonstrates three peaks of zinc, oxygen and carbon, with elemental ratio (72, 22 and 5.18) % respectively [4]. The presence of the carbon in the sample is due to the substrate and sticker of the sample during characterization [5].

TABLE 1: THE ATOMIC COMPOSITION OF THE ZNO NANOPARTICLES

Element	Weight%	Atomic%
C	5.18	14.65
O	22.47	47.73
Zn	72.35	37.61

The I-V Characteristics

The DSSC cells constructed on the FTO and ITO substrates were exposed to a 0.55(mW/cm2) neon lamp illumination and the resulting voltage and current were found and the I-V cures were plotted as shown in Figure 6 and Figure 7. Then the maximum current, the maximum voltage, the short-circuit current and the open-circuit voltage for both cells were also calculated.

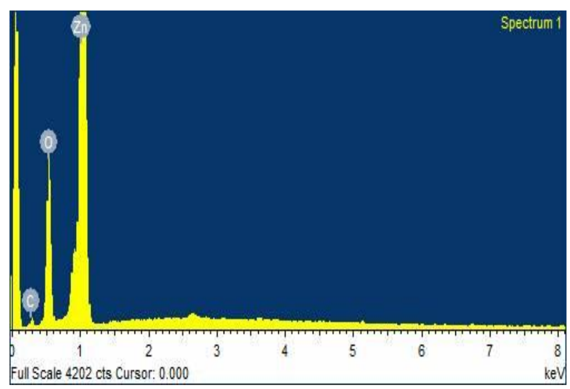

Figure 6: ZnO nanrod EDX spectrum

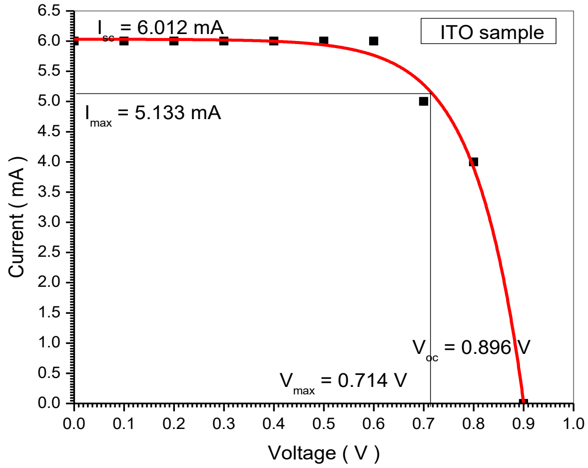

Figure 7: The ZnO-ITO solar cell I-V curve

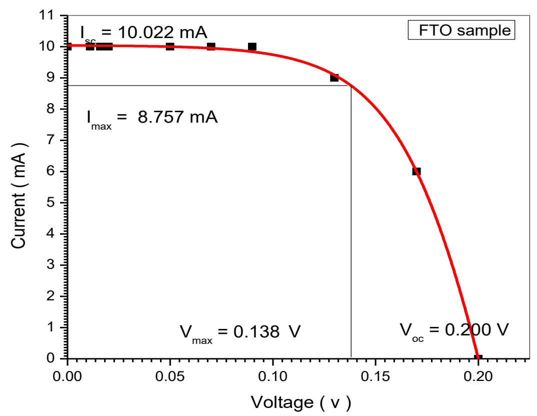

Figure 8: : The I-V curve of ZnO-FTO solar cell

Results and Discussion

The fill factor (FF) was found from equation(4) to be approximately 0.6 for the FTO-ZnO cell and 0.68 for the ITO-ZnO cell. Whereas, the solar to electric power conversion efficiency η, which is ratio of the maximum extractable power to the incident solar power (P_{in}) can be determined from equation (5) and was found to be ~ 1.1% for the ITO-ZnO and ~0.3% for the FTO-ZnO.

$$FF = J_{max}V_{max}/J_{sc}V_{oc} \quad (4)$$
$$\eta = J_{max}V_{max}/P_{in} \quad (5)$$

These results were found to be acceptable when compared to [7] and [9]. But compared to the conventional silicon solar cells which have an efficiency of about 30%, these results are considered very low. Therefore in order to improve these DSSCs, the dye sensitizer used in this research should be changed, also the ZnO nanorods should undergo a doping process to enhance the PV conversion.

CONCLUSIONS

the hydrothermal method was used to synthesize ZnO nanorods in powder form at room temperature. The structural properties were investigated using X-Ray diffraction (XRD) and Fourier Transform infrared (FTIR) spectroscopy. XRD pattern showed that the structure of ZnO is to be crystalline, while EDX studies confirmed the formation of ZnO functional group. The optical band gap energy (Eg) was obtained using UV-VIS-NIR diffuse reflectance spectroscopy. The obtained band gap was approximately 3.41eV and 3.42eV when calculated using two methods and these results attributed to semiconductor behavior. Then The ZnO DSSC were constructed on FTO and ITO substrates, and Rodhamine B dye was used on the both substrates as a dye sensitizer. By comparing the two DSSC solar cells, the ZnO-ITO solar cell was found to be more efficient with efficiency of 1,1% and fill factor of 0.68 while the Zno-FTO had an efficiency of 0.3% and fill factor of 0.6 and this clearly proves that the type of substrate affects the efficiency of the DSSC. Also the dye sensitizer used affected the solar cells efficiency.

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