Mugla Journal of Science and Technology

PHOTOVOLTAIC PRODUCTION TECHNOLOGIES AND ASSESSMENT OF SOLAR CELL EFFICIENCIES FOR NANOSTRUCTURED COBALT DOPED ZINC OXIDES

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Received: 30.05.2015, Accepted: 03.06.2015
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Abstract

In this study, the synthesis and characterization of cobalt doped zinc oxide (Co:ZnO) nanocomposite materials were achieved using hydrothermal method from zinc nitrate and Cobalt (II) chloride precursors. Zinc oxide nanostructures were doped with cobalt in different dopant concentrations. The Co concentration was varied from 0.5 to 1.5 mol % in ZnO crystalline structure. Cobalt doped ZnO materials were analyzed using XRD, SEM and EDX. Also DSSC performances of cobalt doped ZnOs were studied. Best efficiency was obtained with 1% doped Co:ZnO as 3.48 mA/cm^2 of short circuit photocurrent density, 600 mV of open circuit voltage, 0.56 of filling factor, 1.17 of overall conversion efficiency.

Keywords: Photovoltaic production technologies, photovoltaics, ZnO, Co doped ZnO, Solar cell conversion efficiency

KOBALT KATKILI ZnO NANOYAPILAR İÇİN FOTOVOLTAİK ÜRETİM TEKNOLOJİLERİ VE GÜNEŞ HÜCRE VERİMLERİNİN DEĞERLENDİRİLMESİ

Özet

Bu çalışmada Fotovoltaik Üretim Teknolojileri için Kobalt doplu ZnO nanomateryali hidrotermal proses kullanılarak sentezlenmiş ve üretilen fotovoltaiklerin verimleri değerlendirilmiştir. Kobalt doplu ZnO nanomateryaller katkılama oranı % 0.5 den % 1.5'e kadar değişen verimlerde sentezlenmiştir. Katkılanan kobalt doplu ZnO nanomateryaller XRD, SEM ve EDX teknikleri ile analizlenmiştir. SEM görüntüleri kobalt doplu ZnO nanoyapıların morfolojilerinin nanorod düzeyinden nanotabaka morfolojisine değişimini ispatlamıştır. EDX analizleri kobalt doplu ZnO yapıların oluşumunu kanıtlamıştır. Fotovoltaik enerji dönüşüm verimleri analizlenmiştir. Bu çalışmada % 1 kobalt katkılama oranı için 3.48 mA/cm^2 kısa devre akımı, 600 mV açık devre voltajı, 0.56 dolum faktörü ve % 1.17 verim ile en yüksek verim rapor edilmiştir.

Anahtar Kelimeler: Fotovoltaik üretim teknolojileri, fotovoltaikler, kobalt katkılı ZnO, Güneş hücresi dönüşüm verimi

1 Introduction

ZnO is one the nanomaterial employed in dye sensitized solar cells [1, 2]. It is nanoporous semiconductor used as a working electrode for DSSC devices [3]. The band gap and conduction band values of ZnO are similar to that of TiO_2 electrode [4, 5]. The electron mobility, at least in single crystals, is more than one order of magnitude larger in ZnO than in TiO_2 (anatase) [6-8]. Although the many properties of ZnO are similar to TiO_2 nanomaterial, ZnO shows lower efficiency than TiO_2 in dye sensitized solar cells [6, 9]. The synthesis procedure of ZnO is easier than TiO_2. However, ZnO shows poor chemical stability compared to TiO_2. ZnO is a good candidate as working electrode in dye sensitized solar cells (DSSC) because it has similar band gap of TiO_2 and shows lower electron-hole (e^--h^+) recombination probability due to its filled valence band and s-p hybridization properties of conduction band [10] The less population of deep traps in ZnO nanostructures compared to TiO_2 nanoparticles induced the longer lifetime [10]. In spite of these superior physical properties of ZnO, the photoconversion efficiency of TiO_2 based DSSC is generally much higher than ZnO [10].

Since the historic paper on dye sensitized solar cells (DSSCs) was published in 1991 by Michael Graetzel, this area of research has quickly attracted more attention due to their low cost production [11, 12]. Among various metal doped ZnOs, the Co has particular interest due to its various properties like

enhancing the magnetic properties. Previous studies have reported that the microstructure, morphology and Luminescence performance of the Co-doped ZnO (Co:ZnO) materials are extremely sensitive to the condition of their preparation [13-17]. Many synthesis techniques have been developed for the synthesis of cobalt doped zinc oxide materials. Sputtering deposition techniques were widely used for the production processes of nanostructured electrodes. Aqueous solution methods are more favorable for an economical way and large production processes of nanostructured ZnO for photovoltaics. Wet chemical methods have lots of advantages like a controlled growth of crystals. For this reason, hydrothermal methods are considers an effective production technology process of nanostructured transition metal-doped ZnO for photovoltaics [17-19].

In this present study, cobalt doped ZnOs were synthesized using microwave oven by hydrothermal method from zinc nitrate and cobalt chloride precursors. The obtained white-pale greenish precipitate was dried overnight at 80 ^{o}C in hot air oven and desicator. Then, the powder was collected. The resulted Co:ZnO nanomaterials were structurally characterized with various techniques. The Co concentration was varied from 0.5 to 1.5 mol %. The Co doped ZnO materials were analysed with Scanning Electron Microscopy (SEM) Techniques, X-ray diffraction Analysis (XRD), Energy Dispersive X-ray Analysis (EDX). The X-ray pattern clearly showed the presence of crystalline Co:ZnO particles. The scanning electron microscopy analysis confirms that the synthesized Co:ZnO nanomaterials were nanorods in shape and have 79 to 935 nm sizes in length. Performances of Co doped ZnOs were evaluated in dye sensitized solar cells. Under the optimized conditions, 1 % Co doped ZnO gave the best results with the overall conversion efficiency of 1.17 % (η), short-circuit photocurrent of 3.48 mA/cm^2 (J_{sc}), open circuit photovoltage of 600 mV (V_{oc}), fill factor of 0.56 (FF).

2 Experimental Section

All materials were reagent grade and were used as received unless otherwise noted.

2.1. Materials Characterization

The crystalline structures of the Co-doped ZnO samples were determined by XRD studies.
The morphologies of as prepared Co-doped ZnO sample were investigated by SEM(Scanning Electron Microscopy). X-ray diffractometer (XRD) Rigaku with Cu Kα radiation (1.540 Å). was used to characterize the crystal structures of the samples. The operation voltage and current were kept at 40 kV and 40 mA respectively. Philips XL 30S FEG, Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray spectroscopy (SEM EDX) equipment was used the morphology and characterization of the samples. Dye sensitized solar cells were characterized by current-voltage (*J–V*) measurement. All current-voltage (*J–V*) were done under 100 mW/cm^2 light intensity and AM 1.5 conditions. 450 W Xenon light source (Oriel) was used to give an irradiance of various intensities. *J–V* data collection was made by using Keithley 2400 Source-Meter and LabView data acquisition software.

2.2. Synthesis of Co doped ZnOs

Co doped ZnO nanostructures were synthesized by simple hydrothermal process using microvave oven. In a typical synthesis process, zinc nitrate hexahydrate ($Zn(NO_3)_2$. $6H_2O$), cobalt (II) chloride ($CoCl_2$) and NaOH were used. All the chemicals were purchased from Sigma-Aldrich company and used as received. 3.15 mmol $Zn(NO_3)_2.6H_2O$ and appropriate amount of $CoCl_2$ were dissolved by 50 ml distilled water, then 50 ml solution was received, and 37.5 mmol sodium hydroxide (NaOH) was added into the former solution. In the five samples Co:ZnO molar ratios were prepared as 0.5, 1, 1.5 %. And the solutions were stirred by using magnetic stirring. Subsequently, the mixtures were transferred into a teflon-lined vessels, then the vessels were placed into microwave furnace. The mixtures were processed at 195 ^{o}C, 195 PSI, and 1 hour. After the reactions were completed, the teflon lined vessels were removed from the microwave furnace. Then the mixtures were transferred from teflon lined vessels into filtering cones, the mixtures were filtered and the precipitates are collected. Obtained products were washed with pure water several times. Then, pure materials were dried in a furnace at 70 ^{o}C. The as-synthesized materials were investigated in terms of their morphological, structural and dye sensitized solar cell applications.

2.3 Solar Cell Fabrication and Characterization

The counter electrode consisted of FTO (TEC 8; Hartford Glass) catalyzed with platinum (Platisol, Solaronix). Co:ZnO pastes were prepared using dispermat in the ethanol solvent. Co:ZnO coated FTO substrates were immersed in a 0.5 mM solution of the Ru complex of Z907 in ethanol at room temperature overnight, and dried under a flow of nitrogen. The active solar cell area was 0.25 cm^2. The cell was sealed using a Surlyn (60 μm, Solaronix) and the 0.6 M *N*-methyl-*N*-butyl-imidazolium iodide (BMII) + 0.1 M LiI + 0.05 M I_2 + 0.5 M 4-*tert*-butylpyridine (TBP) in acetonitrile as redox electrolyte solution was introduced through pre-drilled holes in the counter electrode. The filling holes were sealed using Surlyn and a microscope cover glass.

3 Results and Discussion

3.1. X-ray Diffraction Analysis of the Co:ZnO materials

The X-ray diffraction (XRD) patterns of the as synthesized Co:ZnO samples were shown in Figure 1. All the diffraction peaks of each sample were well in agreement with JCPDS card of ZnO. These results showed that the as-synthesized Co doped ZnO samples with a hexagonal wurtzite structure. The diffraction peaks positioned at 2θ values of 31.8, 34.5, 36.3, 47.6, 56.6, 62.9, 66.3, 68.0, 69.2, 72.5, 76.9^0 can be indexed to the hexagonal wurtzite phase of zinc oxide (JCPDS card no. 36-1451).

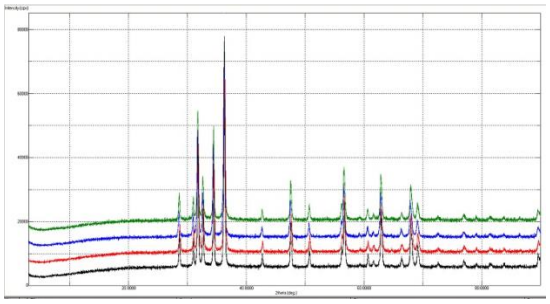

Figure 1. XRD Spectrum of undoped and doped ZnO nanomaterials; undoped ZnO (black), 0.5% doped ZnO (red), 1% doped ZnO (blue), 1.5% doped ZnO (green)

3.1 SEM and EDX analysis of the Co:ZnO materials

The morphologies of as-synthesized Co doped ZnO materials were investigated by using SEM and results were shown in Figure 2-5 (a, b). It was found that morphologies and the length of Co doped ZnO changed by Co dopant. It can be seen that the length of ZnO also changed by increasing Co content. The morphologies of Co doped ZnO nanomaterials changed from nanorod to nanoplate by increasing Co dopant. To check the composion and purity of Co doped ZnO materials were investigated by using energy dispersive X-ray spectroscopy (EDX). EDX spectra were shown in Figure 6. The EDX spectra showed various well defined peaks of Zn, O and Co. No peak related to any other impurity were detected in the spectra. This clearly showed that the synthesized nanomaterials were Co-doped ZnOs.

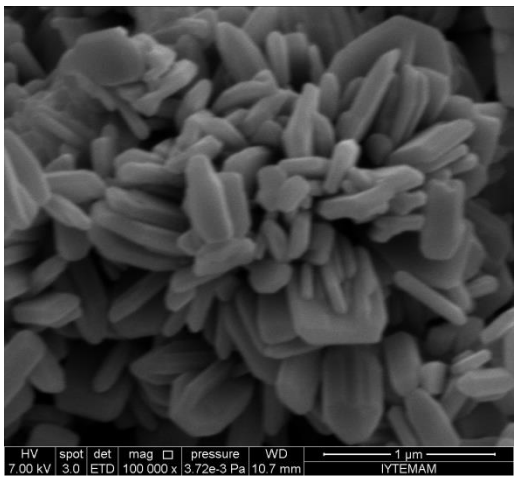

Figure 2. SEM picture of undoped ZnO nanomaterial

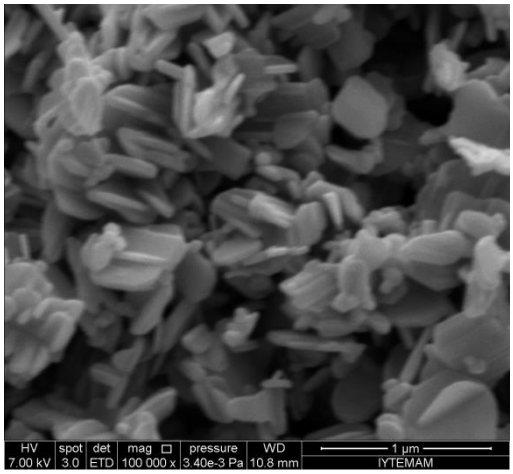

Figure 3. SEM picture of 0.5% doped ZnO nanomaterial

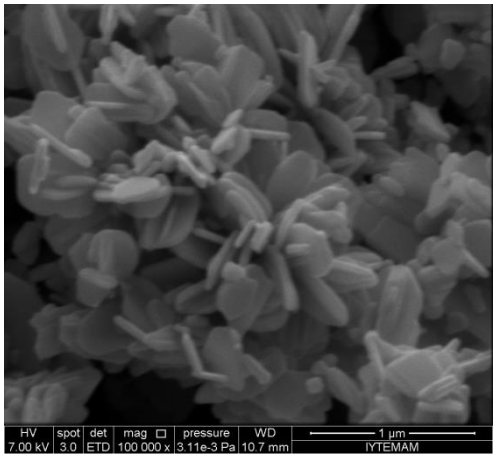

Figure 4. SEM picture of 1% doped ZnO nanomaterial

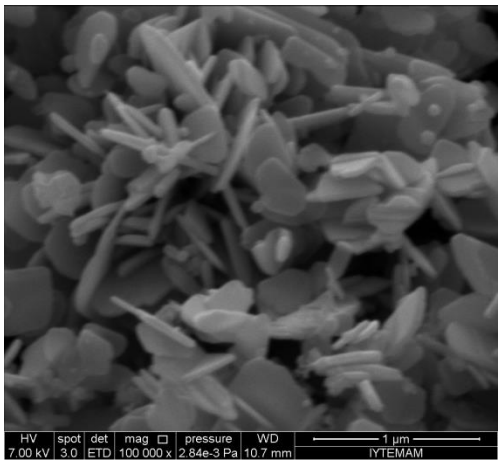

Figure 5. SEM picture of 1% doped ZnO nanomaterial

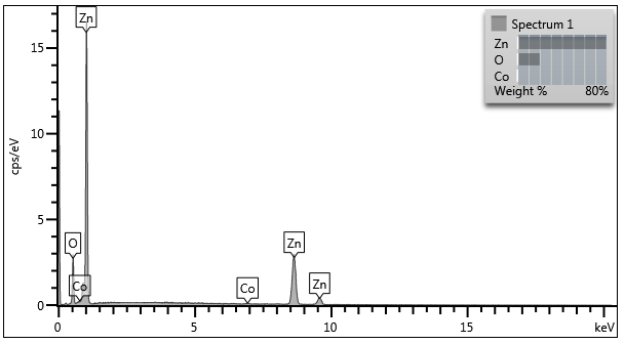

Figure 6. EDX analysis of 1% Co doped ZnO nanomaterial

3.3.Photovoltaic Performances of Co:ZnO materials in DSSCs

Figure 7 illustrated the dye sensitized solar cell using Co doped ZnO materials. The photocurrent density-photovoltage (J-V) and incident photon to current conversion efficiency (IPCE) of DSSCs based on Co:ZnO nanomaterials were presented in Figure 8. And photovoltaic characterization is summarized in Table 1. 1 % Co:ZnO nanomaterial were determined the best performances. Photovoltaic performances were found to increase with an increase in 1% Co concentration. 1 % Co:ZnO exhibits 3.48 mA/cm^2 of current density and 0.56 of overall solar cell efficiency. Whereas 1.5% Co:ZnO shows 2.65 mA/cm^2 of current density and 0.62 of overall solar cell efficiency. Z907 dye is suitable for ZnO material. Under the standard global AM 1.5 solar irradiation, 0.5 % Co:ZnO based DSSC gave a short circuit current density of 2.07 mA/cm^2, open circuit voltage of 600 mV, and a fill factor of 0.62, corresponding to an overall conversion efficiency of 0.78. At the same condition, 1.5% Co:ZnO based DSSC exhibited a a short-circuit current density ($\mathbf{J_{sc}}$) of 2.65 mA/cm^2, open circuit voltage ($\mathbf{V_{oc}}$) of 600 mV, and a fill factor of 0.62, corresponding to an overall conversion efficiency ($\boldsymbol{\eta}$) of 0.1. Solar cell efficiencies changed from 0.78 to 1.17 by changing Co content in the doped ZnO semiconductor. Incident photon to collected electron efficiency (IPCE) of 1 % doped Co:ZnO based DSSC showed 11% efficiency at 500 nm in Figure 8.

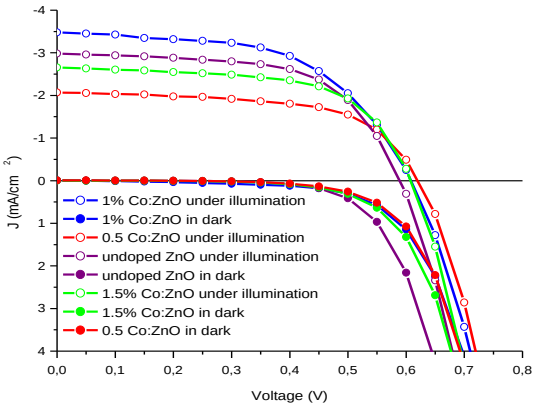

Figure 7. J-V spectra of Cobalt doped ZnO nanomaterials

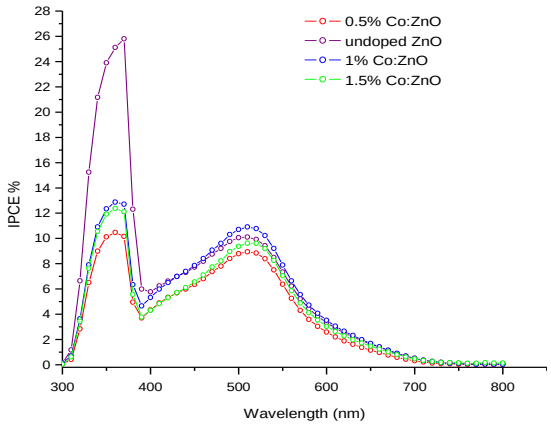

Figure 8. IPCE spectra of Cobalt doped ZnO nanomaterials

Table 1. Photovoltaic Performance of Co:ZnO based Dye Sensitized Solar Cells.

	$\mathbf{J_{sc}}$ (mAcm^{-2})	$\mathbf{V_{oc}}$ (mV)	FF	$\boldsymbol{\eta}$ (%)
1% Co:ZnO	3.48	600	0.56	1.17
Undoped ZnO	2.98	600	0.60	1.07
1.5% Co:ZnO	2.65	600	0.62	1.00
0.5% Co:ZnO	2.07	600	0.62	0.78

4 Conclusion

We have successfully synthesized Co doped ZnO material with the doped concentration from 0.5% to 1.5% Co content. Co:ZnO materials were fully characterized by XRD, SEM and EDX analysis. The photovoltaic performances of Co:ZnO materials were evaluated in DSSCs. It is found that DSSC performances were found to decrease by increasing Co concentration in Co:ZnO materials. Under the standard global AM 1.5 solar irradiation, 1 % Co:ZnO based DSSC gave a short circuit current density of 3.48 mA/cm^2, open circuit voltage of 600 mV, and a fill factor of 0.56, corresponding to an overall conversion efficiency of 1.17.

5 Acknowledgements

We acknowledge financial support from The Scientific and Technological Research Council of Turkey (TUBITAK_114F161), Turkish Academy of Sciences (TUBA), Unesco-Loreal Foundation and especially to Alexander von Humboldt Foundation (AvH).

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