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*Research Article*

# Preparation and Characterisation of ZnO/NiO Nanocomposite Particles for Solar Cell Applications

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The mixture of ZnO and NiO effect on solar cell has been investigated. ZnO and NiO particles were produced by hydrothermal method and the produced particles were annealed at 500°C for 1 hour. Crystal structure and morphological properties of particles were examined by X-ray diffraction (XRD) and scanning electron microscope (SEM). XRD measurements showed that ZnO particles have a hexagonal wurtzite structure and NiO particles have a cubic structure. SEM results show that both ZnO and NiO particles are the form of nanoparticles. Dye-sensitized solar cells were fabricated by N-719 (Ruthenium) dyes and mixing ZnO/NiO particles in different ratios, 100/0, 50/50, and 0/100. It was observed that the solar cells made with ZnO have the highest performance with the efficiency of 0.542%. In addition, it was observed that when amount of NiO ratio increases in the mixture of ZnO/NiO, the efficiencies of DSSCs were observed to decrease.

## 1. Introduction

Zinc oxide (ZnO), a broad bandgap semiconductor material with an energy gap of 3.37 eV and large excitation binding energy (60 meV), has gained a great amount of attention for its potential applications like chemical sensors, surface acoustic wave filters, light-emitting diodes, transparent conductor, and solar cells, and so forth [1–7]. Some other oxide material is nickel oxide (NiO) which is a semiconductor with broad band gap (3.6–4.0 eV) and is widely used in gas sensing, catalysis, magnetic materials, electrochromic films, and battery cathodes [8–11]. Dye-sensitized solar cells (DSSCs) have also gained common interest in the past years due to their low manufacturing expenditures, easiness of fabrication, and tunable optical features, for instance colour and transparency. Nanostructured metal oxide materials, like ZnO, NiO, $TiO_2$, $SnO_2$, and so forth, are used to fabricate DSSCs [12–16]. There are many ways of producing nanostructure materials [17–21]. Hydrothermal method is one of the best ones to produce nanoparticles since it is not expensive and it is an easy method. ZnO and NiO nanoparticles come out with solar cell applications.

In this study, in order to investigate performance of solar cells, nanostructured composite ZnO/NiO DSSCs were fabricated and the obtained results were compared to ZnO and NiO DSSCs. In literature, although there are many studies related to ZnO/$TiO_2$ DSSCs [22–27], we could not encounter any work related to ZnO/NiO composite DSSCs. For instance, Giannouli [26] investigated the effects of ZnO/$TiO_2$ composite on the efficiency and stability of dye-sensitized solar cells. He observed that the combined properties of the materials used in various multicomponent electrolytes enhance the efficiency of the composite ZnO/$TiO_2$ cells. Similarly, Feng et al. [27] fabricated a DSSC based on ZnO/$TiO_2$ composite nanorods photoanode. They found that the DSSC based on the ZnO/$TiO_2$ composite film photoanode yielded a power conversion efficiency of 4.36%, which is much higher than that of DSSCs based on pure ZnO nanorods (3.10%) and $TiO_2$ nanorods film photoanodes (0.63%). Chiang et al. [28] fabricated a DSSC by depositing a film of $TiO_2$/NiO composite particles, which were prepared by mixing the Ni powder with $TiO_2$ particles. Their study shows that the power conversion efficiency of the DSSC with $TiO_2$/NiO composite particles is 3.80%.

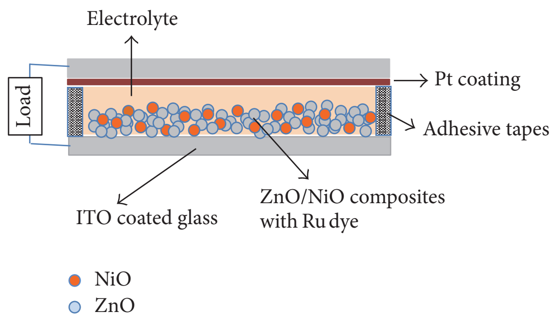



Figure 1: Schematic diagram of the DSSC based on ZnO/NiO nanocomposite particles.

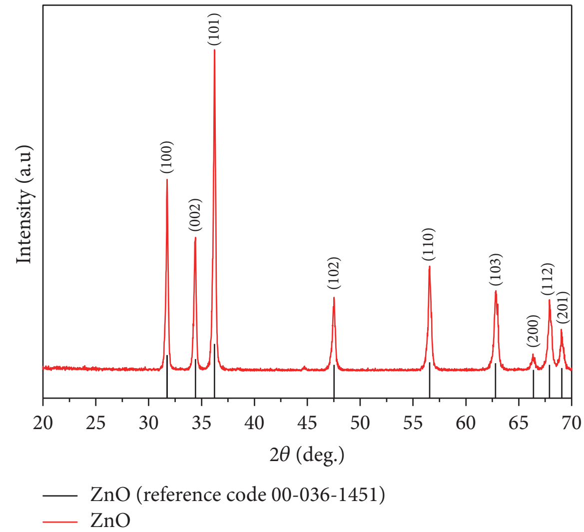



Figure 2: XRD patterns of ZnO nanostructures.

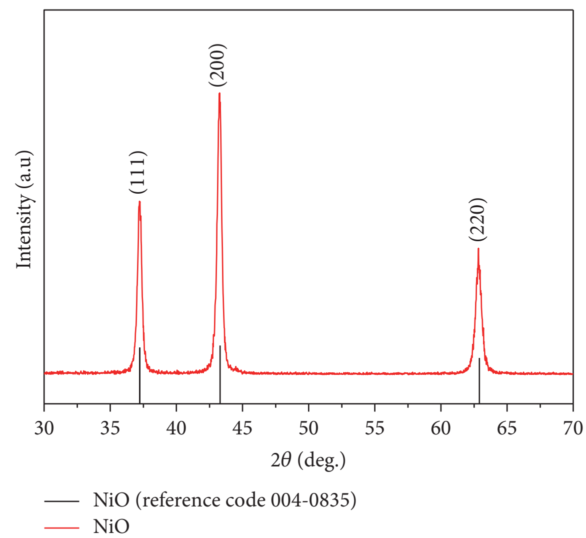



Figure 3: XRD patterns of NiO nanoparticles.

## 2. Materials and Methods

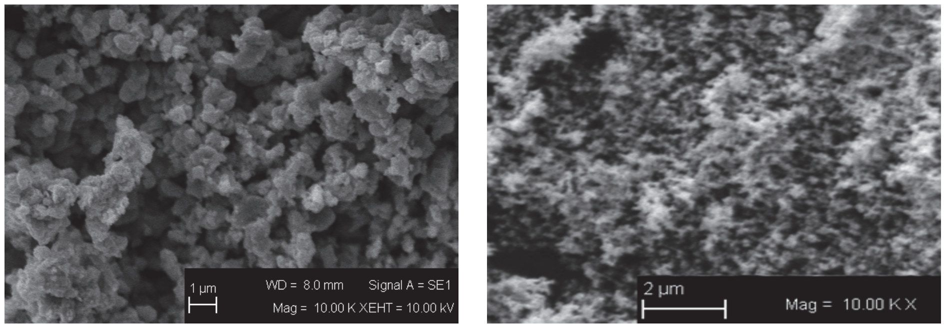
For the synthesis of the ZnO particles, 0.2 M zinc acetate and 0.2 M sodium hydroxide (NaOH) solution are mixed with 50 mL ethanol. The prepared solution is placed in the autoclave and it is waited in furnace at 200°C for 6 hours. NiO was prepared by dissolving 0.1 M of Nickel(II) chloride hexahydrate ($NiCl_2 \cdot 6H_2O$), 0.1 M of hexamethylenetetramine (HMT, $C_6H_{12}N_4$), in 50 mL deionized water. Hydrothermal growth was carried out at 200°C in an autoclave placed in a furnace for 4 h. The obtained particles were washed with distilled water several times and dried at room temperature in air for further characterisation. The obtained particles were annealed for 1 hour at 500°C. Then obtained ZnO particles are mixed with NiO particles. To obtain working electrode of DSSC, ZnO/NiO powder was prepared as a paste and then was printed on ITO glass by using doctor-blading technique. The film thickness was controlled by 3 M adhesive tapes. Finally, the nanostructured ZnO/NiO composite films were dipped into Ruthenium 535-bisTBA dye solutions for 2 hours. Composite thin films containing both ZnO and NiO were prepared by mixing ZnO and NiO particles using dry mixing methods in different ratios: 100/0, 50/50, and 0/100.

The platinum coated counter electrode was prepared by using 10 mM hexachloroplatinic acid ($H_2PtCl_6$) solution in isopropanol. Two to three drops of the solution were dropped on the ITO coated glass plates and after that they were sintered in air at 400°C for 1 h in furnace and cooled down to room temperature in the furnace. The liquid electrolyte was prepared by mixing of 0.5 M KI and 0.05 M $I_2$ dissolved in ethylene glycol. One or two drops of this solution were placed between the working and counter electrode.

The sandwich-type solar cell was assembled by placing a platinum-coated counter electrode on the Ruthenium 535-bisTBA dye-sensitized photoelectrode (working electrode), and they were clipped together as open cells for measurements. A schematic representation of the DSSC based on ZnO/NiO nanocomposites particles is shown in Figure 1. Crystal structure and morphological properties of particles were examined by XRD and SEM. As an application dye-sensitized solar cells were fabricated from nanostructured produced metal oxide particles. *I-V* characteristics of the cells were measured by using Keithley 2400 source meter under the illumination of a 300 watt Xeon lamp using Luzchem Photoreactor calibrated AM1.5 spectrum.

## 3. Results and Discussion

The crystal structure of the particles was determined using X-ray diffraction pattern. Figure 2 shows the XRD patterns of the ZnO nanoparticles. The patterns show peaks appertain to the hexagonal wurtzite ZnO phase. For comparison, the standard powder diffraction data of ZnO (PDF-2 reference code 00-036-1451) is also shown in Figure 2. Figure 3 shows XRD patterns of NiO particles. The patterns show (111), (200), and (220) reflections and all these peaks in the patterns belong to the cubic NiO phase (PDF-2 reference code 004-0835). No other impurity diffraction peaks are observed for ZnO and NiO nanoparticles and the sharp peaks observed from XRD patterns confirm the formation of highly crystalline ZnO and NiO phase.




(a) (b)

Figure 4: SEM images of (a) ZnO hollow spherical nanostructures and (b) NiO nanoparticles.

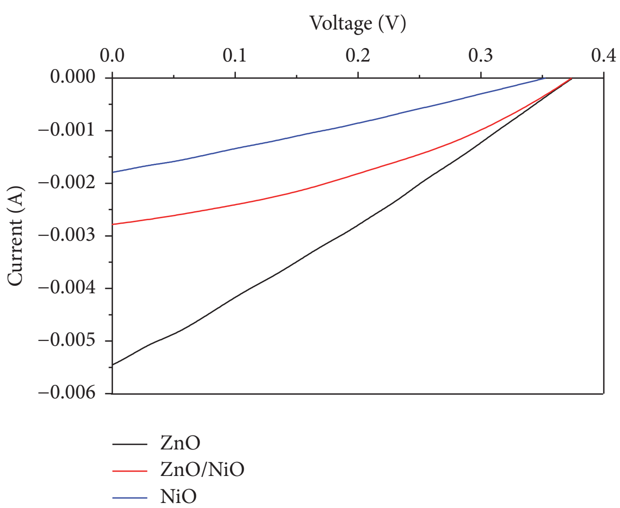



Figure 5: Current-voltage ($I$-$V$) characteristics of ZnO, NiO, and ZnO/NiO DSSCs.

Crystallite size of materials was calculated using the Sherrer's formula as follows:

$$D = \frac{0{,}9\lambda}{\beta \cos\theta}, \quad (1)$$

where $D$ is the crystallite size, $\lambda$ is the incident radiation wavelength (1.5406 Å for Cu K$\alpha$ radiation), $\beta$ is the peak width at its half height in terms of $2\theta$, and $\theta$ is the angle of diffraction. ZnO and NiO average crystallite sizes were found as 47,2 nm and 59,3 nm, respectively. SEM images of the annealed sample are shown in Figure 4. As seen in images, ZnO has hollow spherical nanostructures (Figure 4(a)) and NiO is the form of nanoparticles (Figure 4(b)). From Figure 4 it is observed that the ZnO and NiO nanoparticles are highly porous.

The photocurrent ($I$) and photovoltage ($V$) of the DSSCs were measured under illumination with an active area of 1 cm$^2$ using simulated sunlight at AM-1.5 produced by a 300 W Luzchem Solar Simulator. Photocurrent-voltage curves were obtained with a source meter (Keithley 2400) by voltage linear scanning from 0 V to 0.8 V. The current-voltage ($I$-$V$) characteristics of DSSCs assembled from ZnO/NiO nanoparticle composites were shown in Figure 5. From the $I$-$V$ curves, it was seen that when amount of NiO ratio increases, in the mixture of ZnO/NiO, the efficiencies of DSSCs were observed to decrease.

Table 1: Performance parameters of solar cell.

| ZnO/NiO | $I_m$ (mA) | $V_m$ (V) | $I_{sc}$ (mA/cm$^2$) | $V_{oc}$ (V) | FF | $\eta$ (%) |
|---|---|---|---|---|---|---|
| 100/0 | 2,5 | 0,217 | 5,41 | 0,372 | 0,27 | 0,542 |
| 50/50 | 1,87 | 0,189 | 2,77 | 0,373 | 0,34 | 0,353 |
| 0/100 | 1,08 | 0,155 | 1,79 | 0,36 | 0,26 | 0,167 |

The conversion efficiency is calculated the formula

$$\eta = \frac{P_m}{P_{in}} = \frac{I_{sc} V_{oc} \mathrm{FF}}{P_{in}}. \quad (2)$$

The fundamental results such as a conversion efficiency ($\eta$), an open circuit voltage ($V_{oc}$), a short circuit current density ($I_{sc}$), and a fill factor (FF) have been summarized in Table 1. The fill factor of each cell is calculated according to the following expression:

$$\mathrm{FF} = \frac{I_m V_m}{I_{sc} V_{oc}}, \quad (3)$$

where $I_m$ and $V_m$ are the values of the current and the voltage for the maximum power point, respectively.

In Table 1, even though it was observed that the film made with ZnO has the highest performance, ZnO/NiO composite nanoparticles can provide large surface areas for the dye adsorption. The photovoltaic performances of obtained DSSCs employing ZnO nanoparticles are comparable to published literature [29, 30]. In addition, the $I_{sc}$ and the cell efficiency of the solar cell constructed using NiO are in good agreement with the literature [31, 32]. As seen in Table 1, when ZnO and NiO nanocomposite particles are mixed the efficiency decresases and for the cell made with NiO nanoparticles the efficiency reaches the lowest value. The reason for this is ZnO (hollow structure) dye which is believed to result from better absorption and this increases efficiency.

## 4. Conclusion

ZnO and NiO nanoparticles were produced by the hydrothermal method at 200°C and the obtained nanoparticles were mixed to fabricate the DSSC. XRD and SEM results showed the nanostructure material. From the *I-V* curves, it was seen that when the amount of NiO ratio increases in the mixture of ZnO/NiO the efficiencies of DSSCs were observed to decrease.

## Competing Interests

The authors declare that they have no competing interests.

## Acknowledgments

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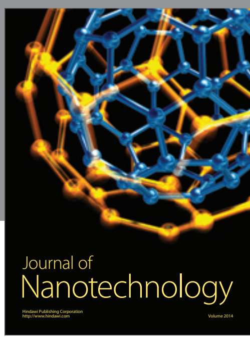
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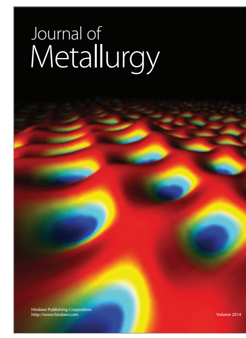
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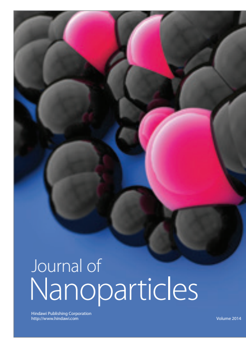
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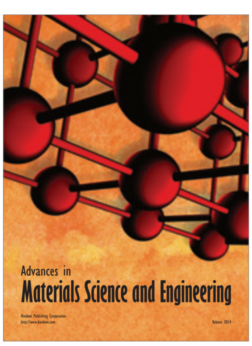
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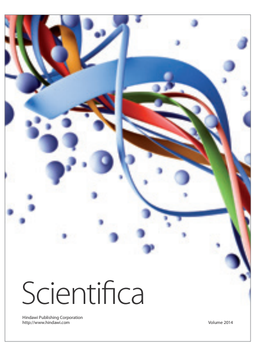
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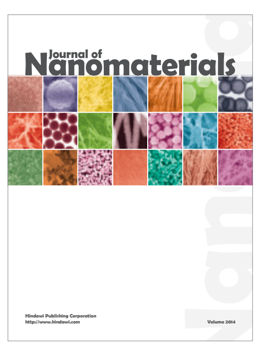
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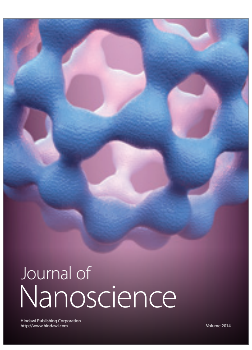
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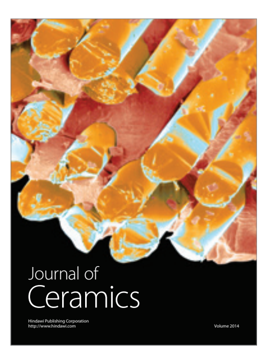
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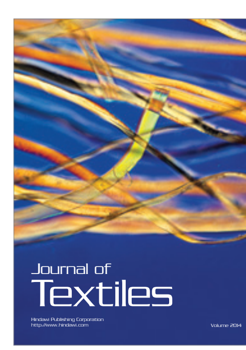
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