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THE EFFECT OF ZnO/NiO NANOCOMPOSITE ON THE PROPERTIES OF A PHOTOELECTRODE OF A DYE SENSITIZED SOLAR CELL

M. SZINDLER*, M. M. SZINDLER
Department of Engineering Materials and Biomaterials, Silesian University of Technology, Konarskiego 18a Str., 44-100 Gliwice, Poland

The aim of the article was to investigate the structure and optical and properties of the ZnO/NiO nanoparticle layer with a different percentage of individual components produced by the sol-gel method. The influence of the developed layers on the properties of dye sensitized solar cells was also determined. Phase identification of the ZnO and NiO samples was confirmed by X-ray diffraction and TEM analysis. From the synthesized nanoparticles, a ZnO/NiO layer was prepared by screen printing method. Studies of the surface morphology of this layer from as prepared nanoparticles, deposited on an FTO glass substrate, was performed by using scanning electron microscopy. Current-voltage characteristics of dye-sensitized solar cells with ZnO/NiO layer and platinum counter electrodes were performed using PV Test Solutions Tadeusz Żdanowicz Solar Cell I-V Tracer System with solar simulator and Keithley 2400 source meter. The best results were obtained for a solar cell containing a ZnO/NiO nanocomposite with 70/30 ratio and its efficiency was 4.46%.

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1. Introduction

Metal nanoparticles and their oxides are obtained in the form of nanocrystals or their agglomerates called clusters. They are nanoscopic three-dimensional systems consisting of several or several dozen atoms of one metal with a dimension not exceeding at least one direction 100 nm and have specific properties. Their unique properties result from the increased density of grain boundaries due to the increase in the specific surface area in a volume unit. For example, reducing the grain size of a given metal from 50µm to 50nm results in a 1000-fold increase in the specific surface area [1-4].

The demand for nanometric structures of metals and metal oxides is growing along with the development of nanotechnology techniques. The area of their applications is also growing. On the priority list of nanomaterials with predicted the largest commercial use in the near future, published as part of the work carried out in the OECD (Inter-Organization Program for the Sound Management of Chemicals - IOMC), the following metals and their oxides have been placed: silver, iron, aluminum, cerium, titanium, zinc or nickel. Nanoparticles are used, among others in the cosmetics, pharmaceutical, automotive and chemical industries (composites, paints, varnishes), construction, electronics, biomedicine and bioengineering, environmental protection and many other. Nanoparticles have properties (physical, chemical, mechanical, optical, electrical, magnetic, etc.) that are different from the properties of their counterparts with a larger particle size. They are characterized by a relatively small mass of particles, developed surface (high surface to volume ratio), significant chemical reactivity and dissolve in liquids differently. Table 1 shows an example of the properties of nano and micro particles of titanium dioxide [5-8].

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* Corresponding author: marek.szindler@polsl.pl

Table 1. Comparison of titanium dioxide properties depending on the size particles.

Properties	**Values depending on the size of the particles**	
Size of particles	0.1÷0.3μm	1÷100nm
Specific surface	~$12m^2/g$	>$300m^2/g$
Absorption of UV radiation	medium	large
Photocatalytic activity	low	high
hydrophilicity	medium	very large
Antibacterial properties	low	high

The ability to produce colloidal particles with the desired physicochemical properties is particularly important for their effective application. The control of the size, morphology and surface properties of nanoparticles can be achieved already at the stage of their preparation. The selection of suitable organic or inorganic stabilizers makes it possible to control the electrokinetic properties of the particles. In addition, the surface functionalization of the nanoparticles can be carried out in a manner that ensures their selective binding to selected target molecules, e.g. drugs or enzymes. On the other hand, for many biological applications, it is desirable that e.g. silver nanoparticles be gradually dissolved and release ions that inhibit the growth and multiplication of bacteria and viruses. In turn, an important issue related to the use of nanoparticles in catalysis is the development of effective methods for their effective deposition on supports, which allows the creation of mono- and multilayers with controlled structure and functionality. The degree of coverage of the surface with nanoparticles and the stability of the created coatings are key factors determining the efficiency and durability of the catalysts produced [9-10].

Techniques for producing nanoparticles can be divided into two groups: bottom-up consisting in building a nanometric structure from individual atoms or particles, and top-down methods consisting in the fragmentation of the micrometric structure to the nanometric scale. The bottom-up techniques include: chemical reduction, sol-gel, photochemical reduction of metal ions using UV/VIS radiation, laser radiation, sonochemical, electrochemical, deposition from the gas phase. For the top down techniques we can include the methods of high plastic deformation and the method of grinding [11-13].

In the article, the sol gel method was chosen as a method for the synthesis of nanoparticles. It is of the greatest importance among methods carried out in the liquid phase. Its advantages include, first of all, the purity of the products obtained, the variety of forms of products obtained, the simplicity of the manufacturing process, as well as the possibility of obtaining products with precisely defined properties, due to the fact that the manufacturing process can be effectively controlled. In this technique, mainly colloidal transition metal oxides are obtained. The essence of this process is the formation usually by hydrolysis, the sol salt of the compound, followed by the slow dehydration of the previously prepared sol leading to its transformation into a gel. In this method the alcoholics hydrolysis reaction is used. The hydrolyzed molecules collide with each other, releasing the water molecule or the hydrolyzed molecule collides with the unhydrolyzed molecule, releasing the alcohol molecule. The rate of hydrolysis and condensation reactions affect the quality of the final material. The hydrolysis stage is the most important, because the slower it is, the smaller particles can be obtained [11-15]. Semiconductor nanoparticles synthesized by the sol gel have found wide application in optics, electronics and photovoltaics. An interesting issue is the use of nanoparticles in third generation of solar cells, specifically in dye sensitized solar cells. The third generation of solar cells offers the prospect of low-cost production of photovoltaic cells with a combination of various attractive properties, such as flexibility, transparency and low toxicity of mainly used materials. It is possible to completely separate from devices with a p-n semiconductor junction by replacing the phase of contact with the semiconductor through the electrolyte, resulting in a photoelectrochemical cell. The dye sensitized solar cell consists of two glasses with a transparent conductive oxide layer (TCO). These layers are part of the DSSC electrodes. On the photoelectrode surface, there is a n-type semiconductor layer with a wide energy gap such as TiO_2, ZnO, Fe_2O_3, ZrO_2, Nb_2O_5, Al_2O_3, CeO_2 Comparison of energy levels and the width of the energy band gap of a variety of materials is shown in Figure 1.

On the surface of the second plate of the TCO glass is usually nanoplatinum constituting a catalyst layer - the arrangement of the solar cell cathode. The space between the plates is filled with electrolyte. Each element of the construction of the dye solar cell affects on its final properties [16-25].

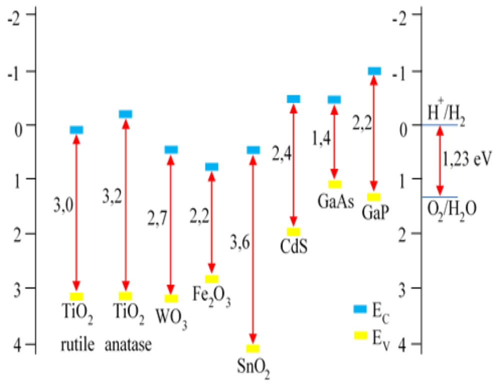


Fig. 1. Comparison of energy levels and the width of the energy band gap of a variety of materials.

In this article the structure and optoelectrical properties of ZnO/NiO nanocrystalline layers was examined, which can be used in dye sensitized solar cells as an alternative to commonly used titanium oxide. The ZnO/NiO nanoparticles layers with a different percentage share of individual components deposited by screen printing on a glass substrate were developed. Their influence on the electrical properties of experimental dye sensitized solar cells was investigated. In literature, although there are many studies related to DSSCs with TiO_2, ZnO or ZnO/TiO_2 [25-29], while only single reports about ZnO/NiO [30] were found, not exhaustive of this topic. The sol-gel method was used to make the proposed particles. The sol-gel method does not require complicated devices and high financial costs, and the creation of nanomaterials does not require high temperature. Thanks to the above-mentioned advantages, the sol-gel method, known for a long time, still constitutes an attractive and modern direction of material engineering development, including primarily surface engineering and nanomaterials.

2. Materials and methodology

The ZnO/NiO nanoparticles were synthesized by using zinc acetate dehydrate (ZnO source) and nickel (II) nitrate hexahydrate (NiO source) as a precursors (Fig. 2).

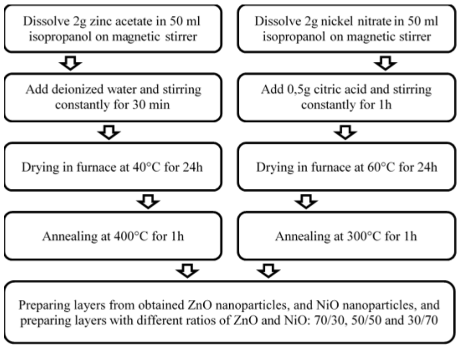


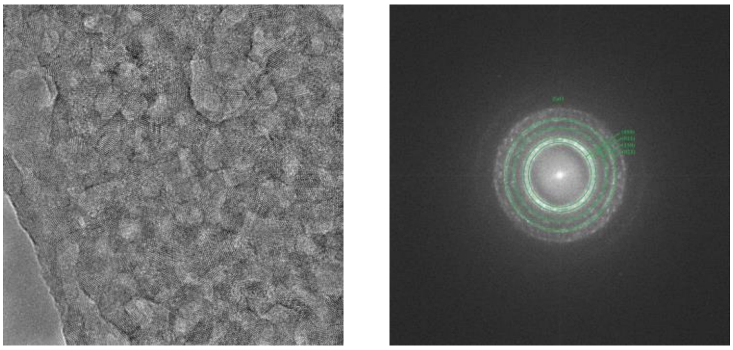
Fig. 2. Schematic diagram of sol-gel processing to obtained the nanoparticles and layers.

For the synthesis of the ZnO particles, a solution consisting of zinc acetate dehydrate and isopropanol by using a magnetic stirrer was prepared. At the same time, solution of the deionized and distilled water was prepared. These solutions were mixed with a magnetic stirrer at temp. 40°C for 20 hours. To evaporate the rest of water, the calcination process was carried out, by heating the chemical compound below its melting point. To synthesis of the NiO nanoparticles, a solution consisting of nickel (II) nitrate hexahydrate and isopropanol by mixing using a magnetic stirrer. After the chemicals had completely dissolved citric acid was added and continued stirring for 1h to allowed complete reaction. The reaction was carried out under room temperature. After the reaction had completed, the solutions will dry in furnace at 60°C for 24h. The resulting material was annealed at 300°C for 1h in furnace. The prepared nanoparticles were subjected to structural analysis using a transmission electron microscope (TEM). Observations were carried out with energy 300kV in the classical model (TEM).
The layers from obtained ZnO nanoparticles, and NiO nanoparticles, and layers with different ratios of ZnO and NiO: (70/30, 50/50 and 30/70) were prepared. To obtain working electrode of DSSC, ZnO/NiO nanopowder was prepared as a paste and then was printed on FTO glass by using screen printing method. Scanning Electron Microscopic (SEM) images were taken with a Zeiss Supra 35. Qualitative studies of chemical composition were also performed using the Energy Dispersive Spectrometer (EDS). The structure of zinc oxide was investigated by X-ray crystallography. The absorbance of nickel oxide layers with dye were measured by Thermo Scientific Evolution 220 spectrophotometer equipped with a xenon lamp in the wavelength range from 190 to 1100nm.

Finally, the nanostructured ZnO/NiO composite layer were dipped into commercially available ruthenium complex - bis(2,2'-bipyridyl-4,4'-dicarbonyl) ruthenium cis-diisothiocyanate (II) commonly known as N3. The platinum counter electrode was prepared by using screen printable platinum paste (DyeSol). The sandwich-type solar cell was assembled by placing a platinum-coated counter electrode on the working electrode and they were clipped together. A few drops of EL-HSE high stability electrolyte were placed between the working and counter electrode. Current-voltage characteristics of dye-sensitized solar cells with ZnO/NiO layer and platinum counter electrodes were performed at Standard Test Conditions (irradiance intensity 1000 W/m^2, temperature 25°C, spectrum AM1.5) using PV Test Solutions Tadeusz Żdanowicz Solar Cell I-V Tracer System with solar simulator and Keithley 2400 source meter. The intensity of incident light was calibrated by National Renewable Energy Laboratory NREL – certified silicon reference cell equipped with KG5 filter.

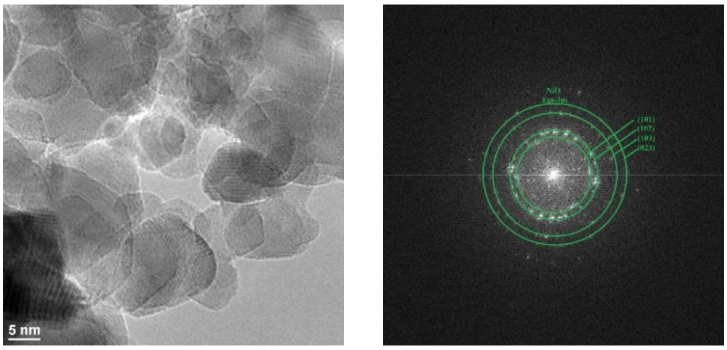
3. Results and discussion

As a result of the synthesis, ZnO nanoparticles not exceeding 10nm and NiO nanoparticles not exceeding 25nm were obtained. It was confirmed by high-resolution transmission electron microscopy. The studied nanoparticles were imaged using high-resolution images (Fig. 3a and 4a). Based on the analysis of high-resolution images by performing a Fast Fourier Transform (FFT), the structure of the produced nanoparticles was determined. The cubic phase of nickel oxide (Fm-3m group) and hexagonal zinc oxide was identified (Fig. 3b and 4b).



(a) (b)

Fig. 3. The HRTEM image of ZnO nanoparticles (a) and it's Fast Fourier Transform FFT (b).



(a) (b)

Fig. 4. The HRTEM image of NiO nanoparticles (a) and it's Fast Fourier Transform FFT (b).

The X-ray qualitative phase composition analysis confirmed presence of ZnO phase based on reflections from plane (010), (002), (011), (012), (110), (112), (021), (023) and presence of NiO phase based on reflections from planes (111), (002), (022), (113) and (222) (Fig 5).

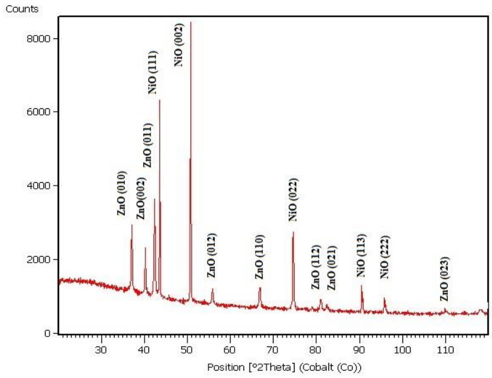
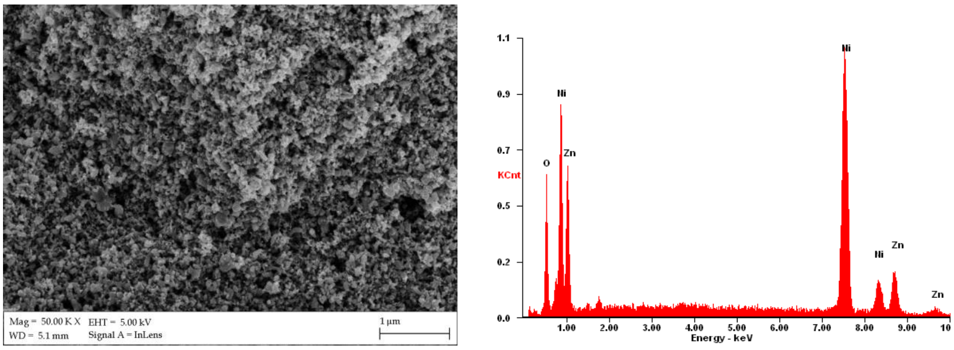


Fig. 5. The X-ray diffraction pattern of ZnO/NiO layer with 50/50 ratio.

Research of the surface morphology of ZnO/NiO layer from as prepared nanoparticles, deposited on an FTO glass substrate, was performed by using scanning electron micrographs and shown in Fig. 6a. It can be seen in figure 6a that the layer is composed of repeating aggregates of ZnO/NiO nanoparticles. In Figure 6b is shown the EDS spectra of ZnO/NiO layer. The peaks assigned to nickel, zinc and oxide from layer were observed.



(a) *(b)*

Fig. 6. SEM image of 50%ZnO/50%NiO layer (a) and it's EDS spectrum (b).

The optical properties of the layers were measured using a Thermo Scientific Evolution 220 spectrophotometer equipped with a xenon lamp with a wavelength range of 190 to 1110 nm. The absorbance A of the ZnO, NiO and ZnO/NiO layers deposited on the glass substrate was measured. Maxima were recorded at wavelengths of around 350 nm (characteristic of ZnO) and at 450nm and 700 nm (characteristic for NiO). The intensity of these maxima was dependent on the percentage of individual components. Increased absorbance in the range 300÷900 nm was registered.

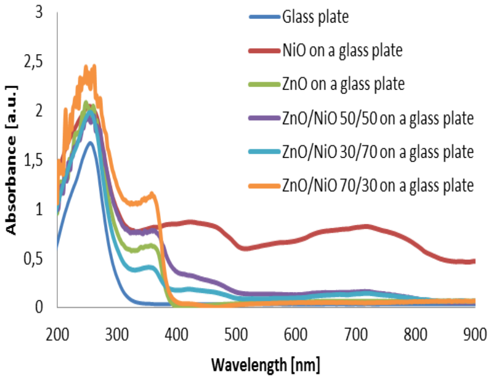


Fig. 7. The absorbance spectrum as a function of wavelength for ZnO/NiO layer.

The current-voltage (I-V) characteristics of DSSCs assembled from ZnO/NiO nanoparticle composites were shown in Figure 8. Among the produced solar cells, the best results were obtained for a solar cell containing ZnO/NiO layer with 70/30 ratio and its efficiency was 4.46%. The result obtained was similar to that of a reference cell containing commercial titanium oxide. A further increase the nickel oxide content in the ZnO/NiO layer caused deterioration of the electrical properties of the solar cell. Explanation of this requires continuing research. The fundamental results such as a conversion efficiency (η), an open circuit voltage (Uoc), a short circuit current density (*I*sc), and a fill factor (FF) have been summarized in Table 2.

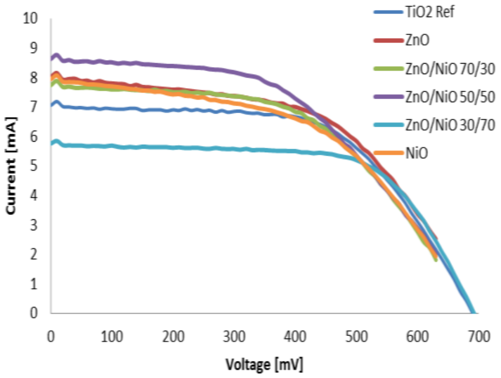


Fig. 8. Current-voltage characteristics of the DSSCs base on ZnO/NiO layer.

Table 2. Electrical parameters of prepared dye sensitized solar cell.

ZnO/NiO	I_M [mA]	U_M [mV]	Isc [mA]	Uoc [mV]	FF [a.u.]	η [%]
100/0	6.34	463	8.02	630	0.589	4.37
70/30	6.40	439	7.72	632	0.577	4.46
50/50	7.02	418	8.63	631	0.540	4.31
30/70	5.09	511	5.76	692	0.653	4.13
0/100	6.08	453	7.94	642	0.550	4.06

4. Conclusions

The uniform zinc oxide and nickel oxide nanoparticles with spherical shape were successfully produced by sol-gel method. The diameter of the as prepared nanoparticles does not exceed respectively 10 and 25nm which is confirmed by the XRD and TEM analysis. The produced nanoparticles have been successfully used as a semiconductor layer in photoelectrode of dye sensitized solar cell.

The electrical properties of experimental dye sensitized solar cells containing the ZnO/NiO layer have been optimized. Among the produced solar cells, the best results were obtained for a solar cell containing a ZnO/NiO layer with 70/30 ratio and its efficiency was 4.46%.

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