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ZnO nanocrystalline powder prepared by sol-gel method for photoanode of dye sensitized solar cells application

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ABSTRACT

Purpose: The article presents the results of research on ZnO nanopowder prepared using sol-gel method that is the easy process enabling us to control shape and size of particles The purpose of this article is to synthesized ZnO nanostructures by sol-gel method and characterized them for use in dye sensitized solar cells.

Design/methodology/approach: Zinc oxide nanopowder was synthesized by using zinc acetate dehydrate as a precursor. The prepared nanopowder has been subjected to structural analysis using a transmission electron microscope (TEM). 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 zinc oxide layers with and without dye were measured by Thermo Scientific Evolution 220 spectrophotometer equipped with a xenon lamp in the wavelength range from 190 nm to 1100 nm.

Findings: Sol-gel method allows the formation of uniform nanoparticles of zinc oxide. The nanoparticles have been successfully used in photoelectrode of dye sensitized solar cell. The light harvesting efficiency of the electrode it remains in a wide spectral range above 85%, which gives better results than in the case of titanium dioxide.

Research limitations/implications: The next step in the research will be to investigate the ZnO/NiO composite on the properties of the photoelectrode of dye sensitized solar cell.

Practical implications: he unique properties of produced ZnO nanostructural materials have caused their interest in such fields as medicine, transparent electronics and photovoltaics.

Originality/value: The ZnO nanoparticles were prepared using sol-gel method and then effectively used in the photoanode of dye sensitized solar cell.

Keywords: Photovoltaic, Dye sensitized solar cell, Sol-gel, Nanoparticles

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PROPERTIES

1. Introduction

Semiconductor nanoparticles based on metal oxides have found wide application in optics, electronics and photovoltaics. One of the interesting top materials in these areas is zinc oxide. The interest in this semiconductor from group II-VI has grown significantly in recent years [1,2]. It is determined by its unique physicochemical properties. Zinc oxide is a material characterized by a wide energy band gap (3.37 eV), with specific optoelectrical properties that allow successful use in touch screens, photodetectors, optical elements and solar cells [3]. Zinc oxide has 3 variations of the crystal structure: hexagonal-wurcite. (Fig. 1), regular zinc blends and rarely observed regular-like NaCl. The hexagonal structure is the most stable and the most common. Zinc and oxygen are coordinated tetrahedral. The lattice constants of the hexagonal ZnO are a = 3.25 Å and c = 5.2 Å and their ratio c/a ~ 1.60 is close to the ideal value of the hexagonal cell c/a = 1.633 [4].

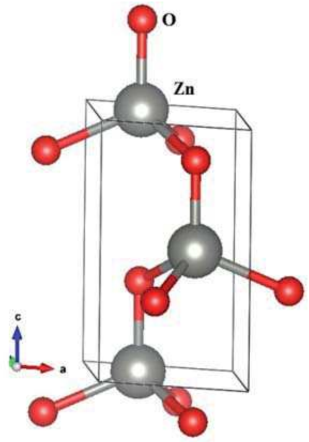

Fig. 1 Structural unit cell of ZnO wurcite

The unique properties of ZnO nanostructural materials have caused their interest in such fields as medicine, transparent electronics and photovoltaics. The research into the application of thin zinc oxide layers has been intensively studied since the 1960s, and later expanded to include nanostructures of various forms. The study of one dimensional (1D) materials has become a prominent in nanomaterials science in the last few decades. The fabrication of metal oxide nanoparticles with particular properties is attracting much attention due to the easy adaptation of the product to the requirements. There are a lot of methods that have been used for fabrication of these materials: chemical vapour deposition, physical vapour deposition, pyrolysis in the vapour phase, hydrothermal, sonochemical, mechanical milling (top down method) and sol-gel [5,6]. The sol–gel method has gained much interest among researchers as it offers controlled nanostructure size and morphology and low processing temperature as compared to other methods (Fig. 2) [7-9].

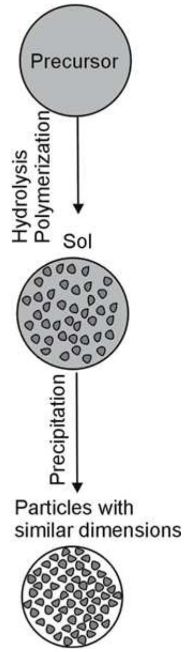

Fig. 2. Schematic diagram of sol-gel processing to obtained the nanoparticles

The ZnO can be an attractive alternative to the titanium oxide used in dye sensitized solar cell when converting solar to electric energy. It's has the same electron affinities and almost the same band gap energies and additionally has much higher electron diffusivity than TiO_2 and has a high electron mobility of 115–155 $cm^2\ V^{-1}\ s^{-1}$, which is beneficial for efficient electron transport in the semiconductor and for reduction of recombination rate [10-12]. In 1976 was developed a working photovoltaic cell based on porous ZnO using a classic Pt counter electrode and iodide/triiodide electrolyte-based redox couple. In the next few years a lot of essential research was done, but the efficiency of these solar cells was low. The next innovation was in 1985, Desilvestro et al. fabricated a TiO2-based photoanode sensitized with a ruthenium-based dye with enhanced photoconversion efficiency. After that in a major breakthrough, in 1991, O'Regan and Grätzel prepared TiO_2-based dye-sensitized solar cells with 7.1% photoconversion efficiency. Since then, a number of metal oxides, sulfides, and selenide semiconductor nanomaterials were tested [13-16].

2. Materials and methodology

Zinc oxide nanopowder was synthesized by using zinc acetate dehydrate as a precursor. First has prepared a solution consisting of zinc acetate dehydrate and isopropanol by mixing using a magnetic stirrer. 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. The prepared nanopowder has been subjected to structural analysis using a transmission electron microscope (TEM). TEM investigations have been performed with a field-emission transmission electron microscope (FEI Titan 80-300 TEM/STEM) with a supertwin lens operated at 300 kV and equipped with an annular dark-field detector. Observations were carried out with energy 300 kV in the classical model (TEM) and in the beam surface-scanning mode (STEM). For this purpose, prepared nanopowder have been deposited on the special copper mesh preparations used in an electron microscopy. Then, zinc oxide thin films from as prepared nanopowder was deposited on an FTO glass substrate by using a doctor blade technique. For this purpose, a paste for doctor blade method was prepared from synthesized nanoparticles. Using an agate mortar, agglomerated nanopowder was triturated. Ethyl alcohol and polyethylene glycol were then added in appropriate proportions and mixed. The prepared paste was deposited with a doctor blade method on a glass substrate with a FTO layer. The prepared layers were heated at 400°C for 1 hour to remove the organic components of the paste. 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. Then a dye was deposited on the prepared substrate. As the dye, a commercially available ruthenium complex was used – bis (2,2'-bipyridyl-4,4'-dicarbonyl) ruthenium cis-diisothiocyanate (II) commonly known as N3 in the form of powder (Sigma aldricht). For the preparation of 25 ml of the N3 dye solution, 8 mg of N3 powder was weighed and dissolved in 15 ml of ethanol, followed by a volume up to 25 ml. The mixture was stirred until the powder was completely dissolved in ethanol. The solution was subjected to ultrasound. The electrode was immersed in the N3 dye in a vessel with the semiconductor layer facing upward for a period of 24 h at room temperature, without access to light. The electrode was removed from the dye solution and washed thoroughly with ethanol to remove excess dye The absorbance of zinc oxide layers with and without dye were measured by Thermo Scientific Evolution 220 spectrophotometer equipped with a xenon lamp in the wavelength range from 190 nm to 1100 nm. As a reference sample, a photoanode with TiO_2 nanoparticles was made. Light harvesting efficiency LHE was calculated using the following formula:

$$LHE(\lambda) = 1 - 10^{-A(\lambda)} \quad (1)$$

3. Results and discussion

The structural studies of as-prepared zinc oxide nanopowder were performed by using S/TEM. The HRTEM image documents the polycrystalline structure of ZnO (Fig. 3). The diameter of the nanoparticles does not exceed a 10 nanometers. In the study, the STEM imaging mode also was used. Titan 80-300 microscope is equipped with a three coaxial detectors dedicated to STEM mode: bright field – BF, annular dark-field – ADF and High angle annular dark-field – HAADF. Images, complementary with the HRTEM mode are shown in Figures 4a and 4b.

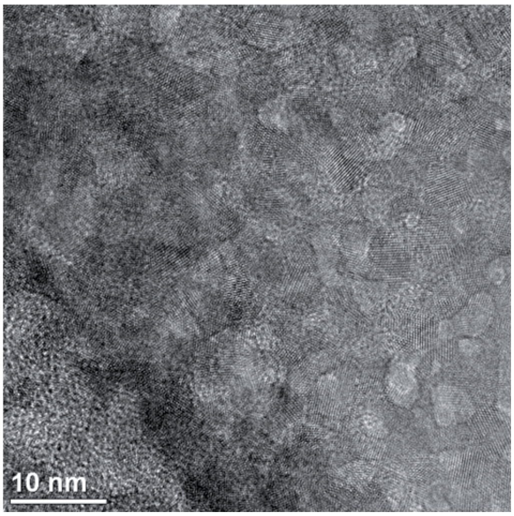

Fig. 3. HRTEM image of the produced zinc oxide nano-particles

Using an energy dispersion spectrometer (EDS), the reflection characteristic for the copper (from the substrate) and the zinc and oxygen (from the sample) was documented (Fig. 5). Studies of the surface morphology of zinc oxide layer from as prepared nanopowder, deposited on an FTO glass substrate, was performed by using scanning electron micrographs and shown in Figures 6a and 6b. It can be seen in figure 4a that the layer is composed of repeating aggregates of ZnO nanoparticles with a sub-micrometer size. These aggregates reach sizes with diameters ranging from several dozen to several hundred nanometers.

a) b)

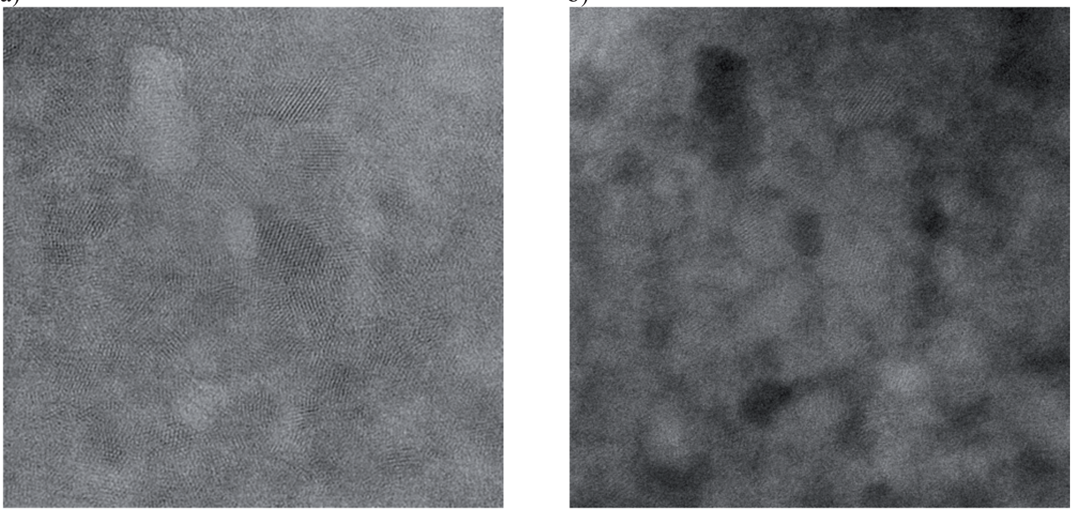

Fig. 4. Image of the produced zinc oxide nanoparticles: a) BF_DF; b) HAADF

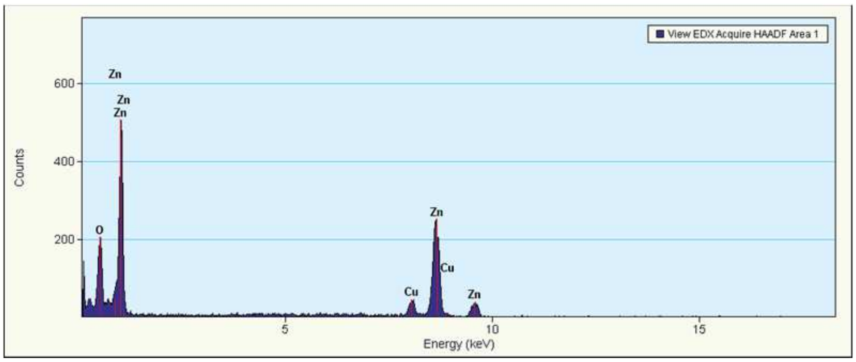

Fig. 5. EDS spectrum of ZnO nanoparticles

a) b)

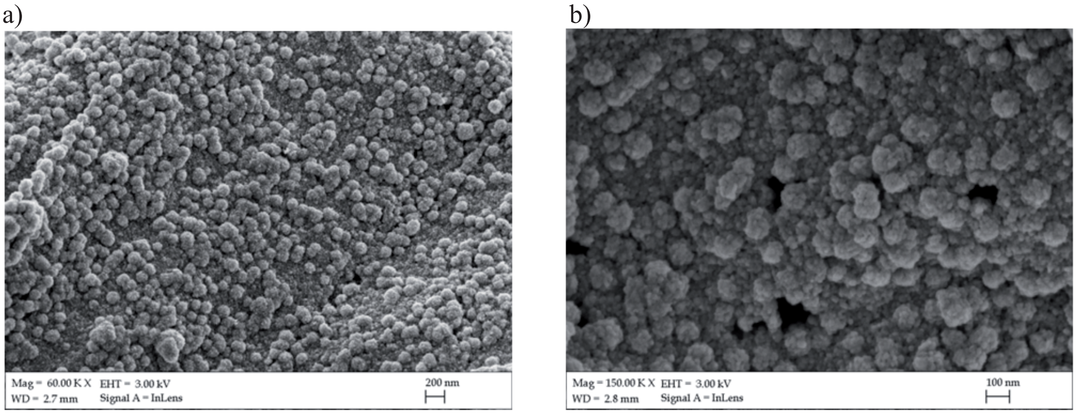

Fig. 6. SEM images of the surface topography of ZnO layer deposited on FTO glass substrate at 60kx (4a) and 150kx (4b) magnification

The high-magnification SEM image shows that ZnO aggregates have an almost spherical shape and consist of nanoparticles. In Figure 7 is shown the EDS spectra of ZnO layer. There are observed peaks assigned to oxygen and zinc from layer and oxygen and tin from FTO layer of glass substrate. Such an analysis can be confirmed the presence of zinc oxide.

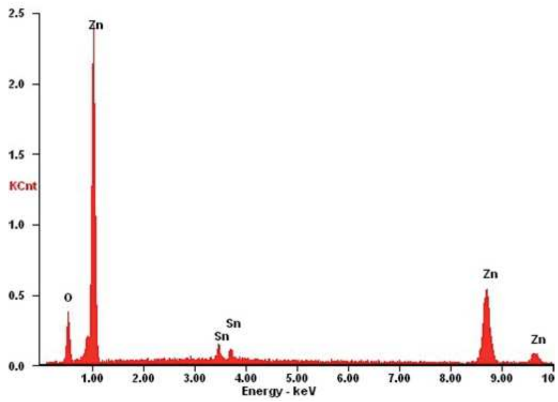

Fig. 7. EDS spectrum of zinc oxide layer deposited on the FTO glass substrate

The structural studies were implemented by using X-ray researches (Fig. 8). Registered diffraction pattern shows the reflections characteristic for the zinc oxide – a hexagonal structure (coming from the sample) and reflections characteristic for tin dioxide – a tetragonal structure (coming from the FTO layer of glass substrate).

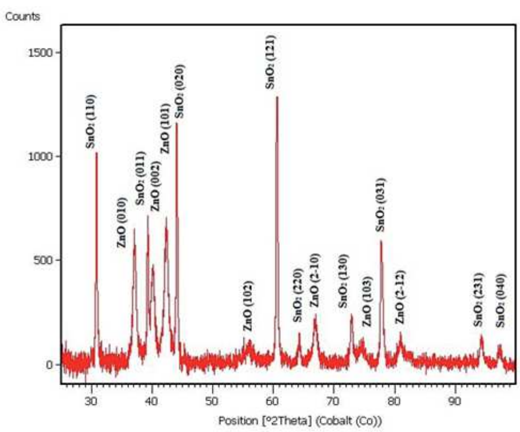

Fig.8. The diffraction pattern of zinc oxide layer deposited on the FTO glass substrate

The titanium dioxide has a high absorbance of light in the UV range, but weakly absorbs visible light, close-up to zinc oxide (Fig. 9). Although the maximum absorbance is higher for titanium oxide than for zinc oxide, zinc oxide in a wider spectral range maintains effective absorbance, even to 380 nm. The adsorption of N3 dye onto a titanium dioxide has increased the absorption in the visible range. In the absorption spectra of the dye layers, there are additional absorption bands that testify to visual transitions in which the charge is transferred from the highest occupied molecular orbital to the lowest unoccupied molecular orbital. Visible absorbance values show that the ZnO layer significantly more deposited the dye than on the titanium oxide. Visible absorbance values show that much more adsorbed the dye on the ZnO layer than on the titanium oxide.

Figure 10 shows the light harvesting efficiency calculated for individual layers of the photo anode of dye sensitized solar cell from equation (1). Titanium dioxide has a high light absorption efficiency in the 200-360 nm wavelength range (above 85%), while zinc oxide between 210-390 nm. Sensitization of the titanium dioxide and zinc oxide layers, deposited on the FTO glass, with the N3 ruthenium complex increases the light absorption efficiency also in the visible range.

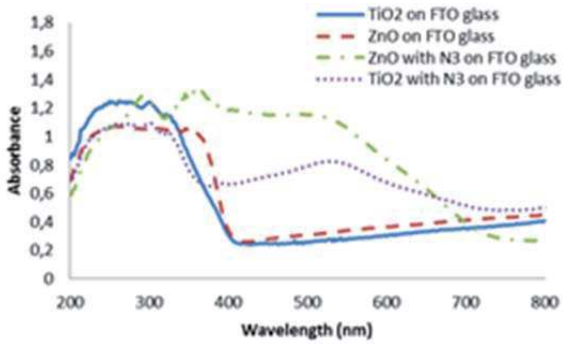

Fig. 9. The absorbance spectrum as a function of wavelength for TiO_2 and ZnO with and without N3 dye

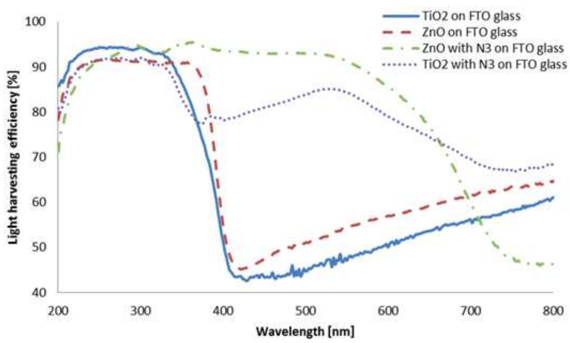

Fig. 10. Light absorption efficiency spectra for individual layers of the photo anode of dye sensitized solar cell

4. Conclusions

Sol-gel method allows the formation of uniform nanoparticles of zinc oxide. The diameter of the as prepared nanoparticles does not exceed 10 nm. The nanoparticles thus produced have been successfully used as a semiconductor layer in photoelectrode of dye sensitized solar cell. The light harvesting efficiency of the electrode it remains in a wide spectral range above 85%, which gives better results than in the case of titanium dioxide.

Acknowledgements

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