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SYNTHESIS OF ZnO-Ag NANOPARTICLES BY SOL-GEL METHOD

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Abstract: Zinc oxide is a highly applicable semiconductor material. Wide application of this nanomaterial is connected to wide spectrum of energy band gap, high bond energy, great thermal conductivity, but also with its non-toxicity, antibacterial activity, biocompatibility and biodegradability characteristics. The aim of this paper is synthesis and characterization of silver doped ZnO nanoparticles (ZnO:Ag NP) using sol-gel method. Obtained samples of silver doped ZnO nanoparticles were characterized by following techniques: Fourier-transform infrared spectroscopy (FTIR), UV/VIS spectrophotometry, X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX). Efficiency of provided synthesis method was examined by FTIR spectroscopy. XRD determined the purity and crystallinity, and wurtzite structure of synthesized material. Surface morphology and the effect of doping were examined using SEM and EDX characterization methods. Results showed better conductivity after doping ZnO nanoparticles with silver. SEM micrographs showed ZnO:Ag NP in the form of nanorods with a particle average size of 6 nm.

Keywords: ZnO, nanoparticles, sol-gel method, nanorods.

1. INTRODUCTION

In the last decade, synthesis of metal nanoparticles with specific and unique properties is a research area that attracts a great deal of attention [1]. This has led to the development of a great variety of techniques for synthesizing nanocompounds like sol-gel, solid state method, hydrothermal synthesis, electrospinning, electrodeposition, laser pyrolysis in the vapor phase, arc discharge, chemical vapor condensation, pyrolysis, thermal evaporation and much more [1,3]. The selection of synthesis method is closely related to the desired properties of material. For experimental conditions, researchers around the world mainly use chemical methods, because these methods allow a direct influence on the desired properties of the synthesized material. What will be a synthesized material, depends on its "attractiveness". Owing to the fact that we live in the era of high tech and electronics, attractive materials are always conductors and semiconductors [1,2]. It is already known that the semiconductor properties of some material can be improved by doping with metal ions [2].

The aim of this research paper was synthesis of silver doped zinc oxide nanoparticles by using sol-gel method. Thanks to its unique physical and chemical properties such as high chemical stability, high electrochemical coupling coefficient, broad range of radiation absorption and high photostability, zinc oxide (ZnO) is a widely used, multifunctional material [4], thanks to the fact that thousands tons of zinc oxide are produced every year for different purposes. The wide implementation is based on good characteristics of this material such as the high index of refraction, thermal conductivity, non-toxicity, antibacterial activity and protection of UV radiation [4]. Thanks to all these characteristics, zinc oxide is used for emitters of ultraviolet radiation, the varistor, the piezoelectric converters, the aeriform sensors, the surface of acoustic wavelike devices, then in transparency of high energetic electronics and in many electronic devices [5]. Zinc oxide belongs to the group of the *n*-semiconductor materials type II^b –VI and some of the most important characteristics of this material are: wide spectrum of energy band gap (≈ 3.4 eV), high bond energy (≈60 meV) and high thermal and mechanical stability at room temperature. On the basis of all these properties, this material can be used in optoelectronic devices, the surface of acoustic-wavelike devices, the emitters of field, light emitter (LED diode), the piezoelectric transformers, chemical, gas and biosensors, the transparency conducting materials, the

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varistors, the solar cells, etc. [5,6]. Further, zinc oxide, because of its non-toxic, antibacterial properties and protection of UV light is used as an ingredient in many pharmaceutical and cosmetic products [6].

The aim of this paper was synthesis of ZnO:Ag nanoparticles by using classic sol-gel method. We examined efficiency of the synthesis method, semiconductor properties of doped and undoped material, surface morphology and silver doping effect.

2. EXPERIMENTAL

Zinc Acetate Dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$, Sigma-Aldrich) ≥99%), Methanol (CH_3OH ≥99%, Merck), Sodium Hydroxide (NaOH ≥97%, Sigma Aldrich) and Silver nitate ($AgNO_3$, Sigma Aldrich) were used for sol-gel synthesis of ZnO NP and ZnO-Ag NPs.

2.1. Synthesis of ZnO and ZnO:Ag nanoparticles

A proper amount of zinc acetate was dissolved in methanol and stirred for 10 minutes on a magnetic stirrer at room temperature. After adjusting the pH value between 10 and 11 by adding NaOH, the sol was gelatinized at 80 °C under constant stirring. Obtained sample, a pure, undoped zinc oxide, is dried for 5 hours at 70 °C, and then calcinated for 3h at 300 °C. The initial temperature was set to 50 °C and then temperature was slowly raised up to 300 ºC (approximately 3 °C/min) in order to avoid overheating and eventual mass losses. The resulting nanopowder was then dispersed in 10 mL of deionized water and stirred on a magnetic stirrer for next 2 h. For incorporation of silver ions, 0.014 g $AgNO_3$ was added to the solution and the solution was constantly stirred vigorously for 4h. By this procedure, obtained ZnO nanopowder was doped with silver ions. The resulting sample is then dried for 5 hours at 70 °C and again calcinated 3h at 300 °C to predict eventual impurities. Such obtained zinc oxide, nanopowders (undoped and doped) were submitted to further characterization.

3. RESULTS AND DISCUSSION

3.1. Characterization of ZnO:Ag nanoparticles

Detailed characterization of doped and undoped ZnO nanoparticles, using following techniques: FTIR, DRS, XRD, SEM and EDX was performed. Semiconductive properties were examined by using diffusion-reflexion spectroscopy (Perkin Elmer Lambda 25 UV/VIS-DRS). FTIR spectroscopy was used to determine the presence of characteristic peak which corresponds to metal oxide (FTIR, Bruker Tensor 27, ATR mode). For determination of the crystallinity of the samples, we used X-ray structure analysis. For X-ray powder diffraction, samples were prepared as thin film between two polymer slides. The diffraction pattern was recorded in transmission mode on a Stoe Stadi P powder diffractometer with CuKα radiation, λ = 1.5148 Å and a Dectris Mythen 1K strip detector. Scanning electron microscopy (SEM, JEOL JSM-6390 LV) was used for investigation of surface and morphology of samples. The presence of silver nanoparticles onto zinc oxide surface was determined by using EDX (Hitachi SU 8020) technique.

3.1.1. FTIR spectroscopy

In the order to determine characteristic peak which corresponds to ZnO nanoparticles, we performed FTIR spectroscopy in the range from 400 to 4000 cm^{-1}[7]. FTIR spectroscopy is usually the method of choice for characterization of organic compounds, but if we use range below 1000 cm^{-1} it can also be useful for characterization of inorganic compounds [7]. According to literature data [7], characteristic peak of ZnO appears in the range 400-700 cm^{-1} [7,8]. Figure 1 shows the FTIR spectra of zinc oxide synthesized by the sol-gel method. As we can see, a spectrum of undoped ZnO nanoparticles synthesized *via* sol-gel method shows three characteristic bands at the frequencies value 1438 cm^{-1}, 894,02 cm^{-1} and 594, 72 cm^{-1}, while in case of silver doped ZnO, new peak at 466,87 cm^{-1} appears.

According to the literature [9-11], the absorption maximum at 594, 72 cm^{-1} and 466.87 cm^{-1} correspond to the Zn-O bond, while vibration peak on 894,02 cm^{-1} according to the Rene et al., originates from substitution hydrogen at oxygen site (OH) bound to the lattice Zn site (i.e., Zn–HO). This substitutional hydrogen may act as a shallow donor in ZnO [9]. The wide stretched peak in the range from 1000-1500 cm^{-1} belongs to C=O (symmetric and asymmetric stretching) vibrations [9]. As we can see in Figure 1, silver doped ZnO nanoparticles show the higher intensity of absorption and one more vibration band on 466,87 cm^{-1}. Similar was reported by Gayatri et al. Change in the band position towards the lower frequency, which is the case in all our doped samples, can be associated with the bond length changes because of the partial incorporation of Ag^+ ion at the ZnO lattice site [11].

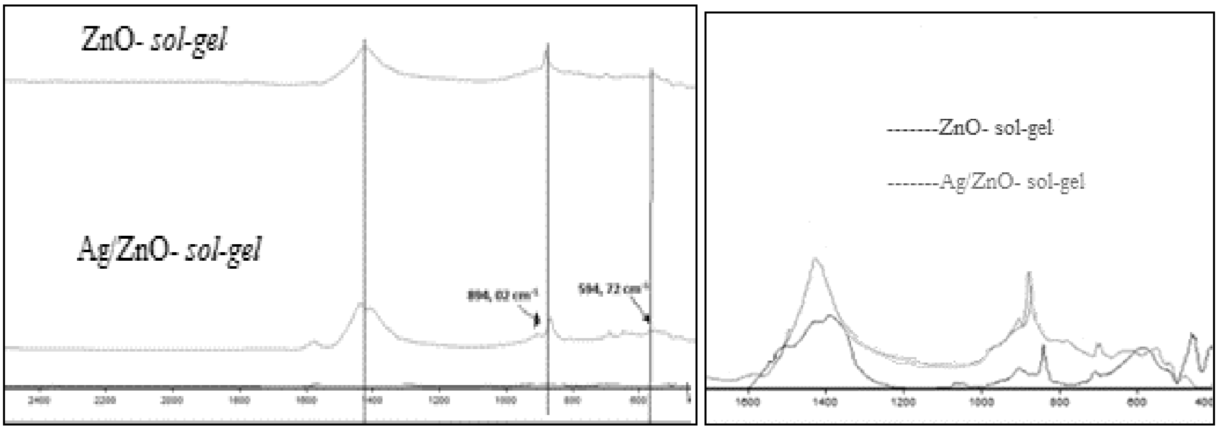


Figure 1. FTIR spectra of doped (ZnO:Ag) and pure ZnO nanoparticles synthesized via sol-gel method

3.1.2. Diffuse reflectance UV-Vis spectroscopy (DRS)

Semiconductor properties of doped and undoped samples were determined based on band gap energy with the help of Kubelka-Munk function. Zinc oxide has 4.17 eV energy of band gap, while silver doped sample has 3.52 eV band gap. Width of band gap is directly related to size of nanoparticles. Note that smaller particles have wider band gap and *vice versa*. Based on experimental data, we can conclude that incorporation of silver ions significantly improves semiconductor properties of zinc oxide nanoparticles.

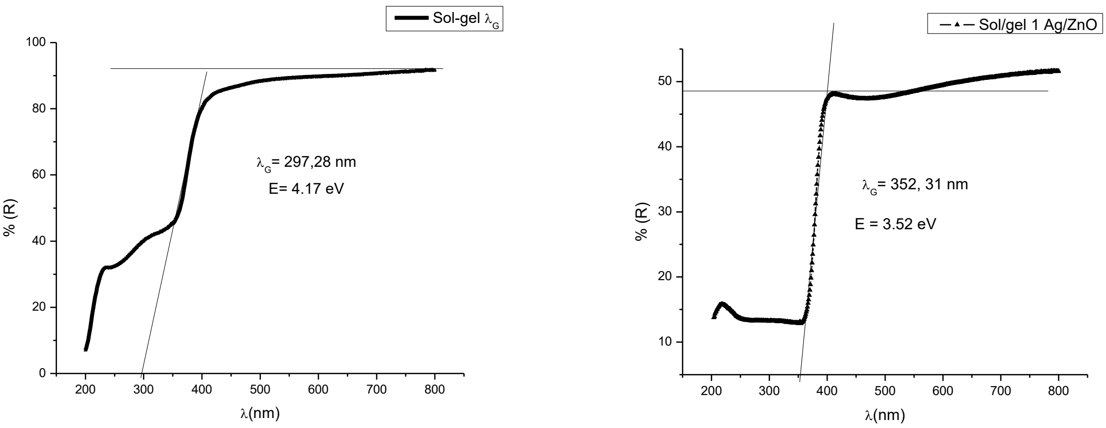


Figure 2. Band gap of ZnO Nps (left) and ZnO:Ag NPs (right) synthesized by sol-gel method

3.1.3. X-ray structure analysis (XRD)

X-ray structure analysis of synthesized samples was applied from 20˚ to 80˚. Based on diffractograms, crystal lattice parameters of nanoparticles were determined: a=2.999 Å and c=6.192 Å. Crystal structure of synthesized samples was determined by software, based on standard of zinc oxide (Figure 3b, red lines). Values of angles were compared to JCPDS standard card [12], (No. 36-1451, Table 1). Diffractograms showed characteristic peaks for planes (100), (002), (101), (102), (110), (103), (200), (112), (201) and (004), and determine the hexagonal wurtzite crystal structure. But, experimental data showed shift of diffraction angle of undoped and doped samples to higher or lower values comparing to standard (Table 1).

Based on experimental data, it is evident that with this synthesis method, one phase material was not obtained, and the influence of the precursor was significant and prevailed. Diffractograms did not showed the presence of peaks which can confirm existence of silver ions in the structure. Due to this conclusion, effect of doping was examined with SEM and EDX methods.

Table 1. 2Θ values of synthesized samples compared to standard of ZnO JCPDS card no. 36-1451 [12]

hkl	(100)	(002)	(101)	(102)	(110)	(103)	(200)	(112)	(201)	(004)
JCPD 36 1451	31,770	34,420	36,253	47,540	56,604	62,865	66,383	67,967	69,103	72,564
ZnO sol-gel	31,745	34,475	36,275	47,540	56,600	62,825	66,355	67,880	69,020	72,485

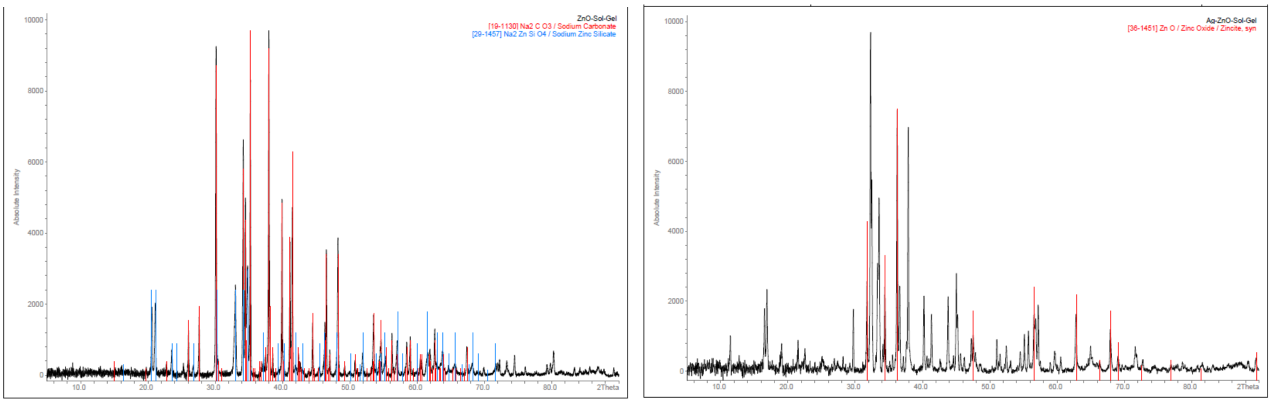


Figure 3. X-ray diffractograms: a) undoped ZnO ; b) silver doped (ZnO:Ag) nanoparticles synthesized by sol-gel method

3.1.4. SEM and EDX methods

Based on the all results so far, none of the previously described methods has given us information about doping effect and because of that we performed SEM and EDX measurements for our doped and undoped samples. These methods determined the morphology of the samples (SEM), and also the qualitative presence of the silver nanoparticles on the surface (EDX). The results show different sizes of the particles and significant effect of agglomeration (Figure 4a and 4b). Further we determined nanoparticles size distribution. For nanoparticles, size distribution ImageJ software was used and results are presented in Figure 2 and Table 2.

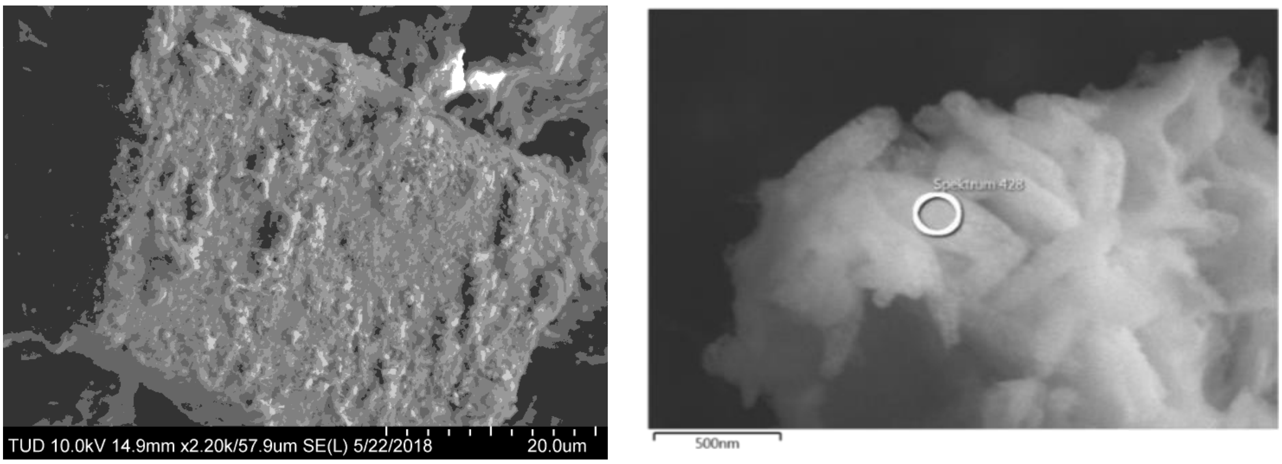
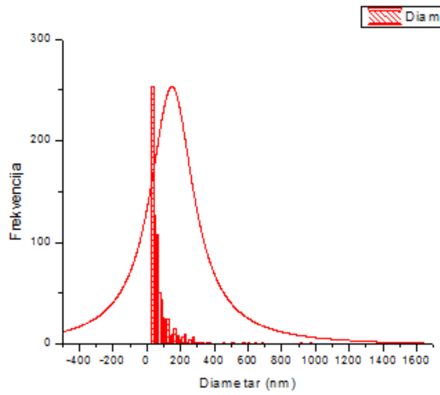


Figure 4. SEM image of ZnO:Ag NP synthesized by sol-gel method



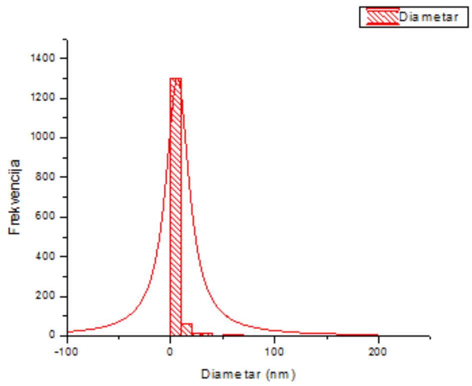


Figure 5. Nanoparticles size distribution according to ImageJ results a) ZnO; b) ZnO:Ag

Table 2. Statistics of nanosized particles distribution

Sample	Mean	SD	Maximum	Number of counted particles
ZnO (X20µm)	137.89934	312.5356	5001.27892	902
ZnO:Ag (X20µm)	247.11964	299.6165	1403	78
ZnO:Ag (X1µm)	6.39726	27.39	927.794	1414

4. CONCLUSION

Aim of this paper was to explore possibility of improvement of semiconductors characteristics of sol-gel synthesized nanoparticles of zinc oxide by incorporation of silver ions. Characterization of investigated samples was performed using various contemporary techniques. FTIR spectroscopy showed the presence of two vibration bands in range 500-700 cm^{-1}, which correspond well to zinc oxide. Experimental data from diffuse reflectance spectroscopy showed better semiconductor properties in silver doped zinc oxide sample based on bang gap. Wurtzite crystal structure was determined in both samples, doped and undoped, with characteristic crystal lattice parameters a = 2.999 Å and c = 6.192 Å. XRD results also showed that these materials are not one-phase materials, because there was detected the presence of precursors. Based on SEM images, nanorods having average size around 6 nm were obtained. EDX experimental method showed qualitative presence of silver ions on the surface of doped sample, which confirms the success of this synthesis method in doping of ZnO nanopraticles. To conclude, sol-gel method is a good choice for synthesis of semiconductor materials in form of nanorods, which can be applied in different optical and electrical devices industries. Further improvement of semiconductor properties is the target for our future research.

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СИНТЕЗА ZnO-Ag НАНОЧЕСТИЦА СОЛ-ГЕЛ ПОСТУПКОМ

Сажетак: Цинк оксид је мултифункционални, полупроводнички материјал. Велика примјена овог материјала потиче од широког енергетског процјепа, високе вриједности енергије везе, те добре топлотне проводљивости, антибактеријске активности, биокомпатибилности и биодеградибилности. Циљ овог рада била је синтеза и карактеризација сребром допингованих ZnO наночестица (ZnO-Ag NP) употребом сол-гел поступка. Добијени узорци окарактерисани су кроз пет метода карактеризације: FTIR спектроскопија, UV/VIS дифузионо-рефлексиона спектрофотометрија, XRD структурна анализа, SEM и EDX. Ефикасност синтезе узорака испитана је употребом FTIR спектроскопије. Чистоћа, кристаличност и вурцитна структура добијених узорака испитани су употребом рендгенске структурне анализе. Површинска морфологија узорака као и ефекат допинговања испитани су употребом скенирајуће микроскопије и EDX методе карактеризације. Резултати показују боље проводничке способности ZnO наночестица након допинговања сребром и да добијене наночестице кристалишу у форми наноштапића.

Кључне ријечи: ZnO, наночестице, сол-гел метода, наноштапићи.

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