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# Mechanochemical synthesis and properties of $ZnS/TiO_2$ composites

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$ZnS/TiO_2$ composites have been prepared by simple solid-state mechanochemical route. One sample was prepared in a planetary ball mill by dry milling of $TiO_2$ P 25 Degussa with mechanochemically synthesized ZnS (cubic sphalerite phase, JCPDS 00-05-0566) in advance. Another sample has been obtained by the wet mechanochemical synthesis from zinc acetate and sodium sulfide in the presence of $TiO_2$ P 25 Degussa. The phase and structural transformation were studied by XRD analysis. It was established that the dry milling of mixture of $TiO_2$ P 25 and ZnS induced phase transformation of anatase in $TiO_2$ P 25 to rutile. Anatase phase was identified in diffraction pattern of the mechanochemically synthesized sample by wet route. Diffuse reflectance spectroscopy was applied in order to evaluate the band gap energy of the synthesized samples. The properties of the prepared $ZnS/TiO_2$ samples in photocatalytic decoloration of Methyl Orange (MO) dye as model decontaminant in aqueous solution were examined. For determination of the emission behavior of the mechanochemically synthesized $ZnS/TiO_2$ composites, the room temperature photoluminescence (PL) spectra were recorded by exciting the samples with excitation wavelength of 325 nm. The multiple emission peaks were observed. The lower PL intensity of the mechanochemically synthesized $ZnS/TiO_2$ sample by dry route indicates a lower recombination rate of photo-excited electrons and holes.

**Keywords:** mechanochemistry, photocatalysis, titania, ZnS, Methyl Orange

## INTRODUCTION

Various semiconductor materials such as $TiO_2$, ZnO, CdS or ZnS have been employed to study photocatalytic reduction of pollutant in water [1]. $TiO_2$ has been proved to be efficient photocatalyst due to its optical and electronic properties, chemical stability, non-toxicity and low cost [2]. However, in many cases, the photocatalytic activity of $TiO_2$ is not enough to make it applicable for industrial purposes [3]. ZnS is the direct-transition semiconductor with the widest energy band gap among the groups of II-VI semiconductor materials. ZnS based composite materials have been developed in order to extend the utilization of ZnS [4]. In last two decades a variety of methods have been used for ZnS synthesis such as hydrothermal method [5], sol-gel method [6], solvothermal method [7] and mechanochemical synthesis [8]. High-energy milling has been widely applied for the synthesis of nanocrystalline materials [9, 10]. Takacs et al. [11] have investigated mechanochemical formation of Zn, Cd and Sn chalcogenides from a mixture of metals and sulfur powders. Mechanochemical reactions are characterized by repeated welding and fracture of reacting particles during ball-powder collisions, which continually regenerate reacting interfaces. The mechanochemical synthesis for preparation of composites has significant potential for large scale production due to high efficiency and low cost process [9].

In recent years ZnS nanocrystals have been studied due to their interesting properties having potential as photocatalysts in environmental contaminant elimination [12]. Nanoscale ZnS coupled $TiO_2$ photocatalysts have been investigated due to potential applications such as purification of wastewater [13].

In the present work, the mechanochemically synthesized $ZnS/TiO_2$ composites were tested and their photocatalytic activities were compared with data, previously obtained with the traditionally used reference photocatalyst $TiO_2$ Degussa P25. Methyl Orange dye was selected as a model reactant for photodegradation. The aim of the present paper was to investigate the influence of the synthesis conditions for the preparation of $ZnS/TiO_2$ composites by monitoring their optical and photocatalytic properties.

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## EXPERIMENTAL

The $ZnS/TiO_2$ composites were synthesized from zinc acetate $(CH_3COO)_2Zn.2H_2O$ (98 %, ITES, Slovakia), sodium sulfide $Na_2S.9H_2O$ (98%, Aldrich, Germany) and $TiO_2$ Degussa P25.

The mechanochemical synthesis of the samples was realized in a Pulverisette 6 planetary ball mill (Fritsch, Germany) under the following conditions: the ball mill was charged with 50 balls of diameter 10 mm having weight of 360 grams, made of tungsten carbide. The rate of rotation of the planetary carrier was 500 rpm. The milling was performed conducted in inert atmosphere of argon at the room temperature.

Pure zinc sulfide was mechanochemically prepared and was described in our study [14].

The first composite sample was denoted as $ZnS/TiO_2$-1 and it was synthesized by milling in a planetary ball mill using the pure zinc sulfide, prepared beforehand and the commercially available $TiO_2$ P25 Degussa at a ratio 1:4. The milling time was 30 minutes.

The second mechanochemically synthesized composite sample labeled $ZnS/TiO_2$-2 was prepared by milling a mixture of zinc acetate, sodium sulfide and $TiO_2$ P25 Degussa. The synthesis was carried out in the planetary ball mill in inert atmosphere under the same conditions as are described above.

The X-ray diffraction (XRD) patterns were recorded on a D8 Advance diffractometer (Brucker, Germany) using CuKα radiation.

The values of specific surface areas ($S_A$) were obtained by the low-temperature nitrogen adsorption method using a Gemini 2360 sorption apparatus (Micromeritics, USA).

The diffuse reflectance UV–vis spectra for evaluation of photophysical properties were recorded in the diffuse reflectance mode (R) and transformed to absorption spectra through the Kubelka-Munk function [15]. A Thermo Evolution 300 UV-vis Spectrophotometer, equipped with a Praying Mantis device with Spectralon as the reference was used.

The photoluminescence (PL) spectra at room temperature were acquired at right angle on a photon counting spectrofluorometer PC1 (ISS) with a photoexcitation wavelength of 325 nm. A 300 W xenon lamp was used as the excitation source. For measuring the PL intensity, the powders were suspended in absolute ethanol.

The photocatalytic activity of the samples in the reaction of Methyl Orange decoloration was measured under UV-C monochromatic illumination (TUV lamp $\lambda$=254 nm) and under visible light illumination.

The photocatalytic experiments were carried out in a semi-batch photoreactor equipped with a magnetic stirrer, similarly as in the case of our previous work [16]. The suspension was prepared by adding $ZnS/TiO_2$ sample (100 mg) to 100 mL of Methyl Orange (MO) solution with a concentration $1.10^{-5}$ M. The suspension was magnetically stirred in the dark for 30 min to ensure an adsorption-desorption equilibrium. Then the suspension was irradiated by Philips TUV lamp (4 W). UV-C monochromatic radiation is $\lambda$=254 nm. All experiments were performed at constant stirring rate 400 rpm at room temperature. The concentration of MO during the photocatalytic reaction was determined by monitoring the changes of the main absorbance peak at $\lambda$=463 nm.

## RESULTS AND DISCUSSION

The XRD measurements were carried out to study the phase composition of the obtained samples. The XRD patterns of $ZnS/TiO_2$ composites, synthesized by mechanochemical route, are given in Fig. 1. The patterns of the commercial product $TiO_2$ P25 Degussa and mechanochemically synthesized ZnS are also given for comparison. The X-ray diffraction pattern of $TiO_2$ P 25 Degussa shows that it is composed of crystallites of anatase and rutile at a ratio 75:25. Some diffraction lines are observable in the XRD pattern of the ZnS, synthesized by us, which indicate the cubic sphalerite structure (JCPDS 00-05-0566). All diffraction peaks are broadened because of fine size of crystals [17] as well as due to structural disorder introduced into zinc sulfide by milling procedure [9]. The crystallite size of ZnS determined from the Scherrer formula from the major peak centered at $2\Theta=28.8^{\circ}$ was estimated to be about 3.9 nm.

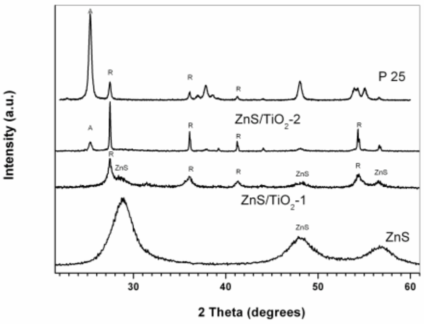
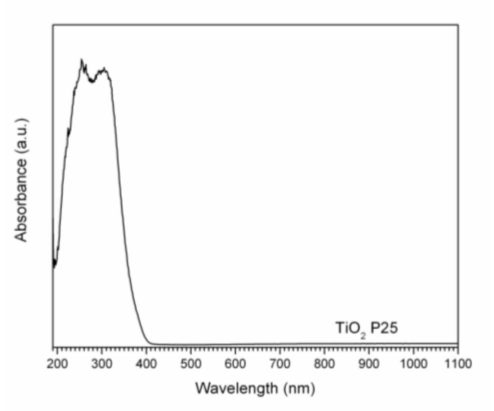


**Fig. 1.** XRD patterns of initial $TiO_2$ P25 Degussa and mechanochemically synthesized samples ZnS, $ZnS/TiO_2$-1 and $ZnS/TiO_2$-2.

Valuable changes were noticed in the XRD pattern of the sample ZnS/$TiO_2$-1 prepared in a planetary ball mill by dry milling of $TiO_2$ P 25 Degussa with mechanochemically synthesized ZnS. The substantial decrease in the intensity of the peaks at $2\theta=27.5^o$, $36^o$, $41^o$ and $54.1^o$ related to the rutile was observed (Fig. 2). No characteristic lines of anatase phase were registered in the XRD pattern of this composite sample. It follows from that phase transformation of anatase into rutile occurred in this case. A significant broadening was observed for all registered diffraction lines. A considerable decrease in the size of the crystallites was observed in this sample. Some lines characteristic of the ZnS were also present. The rutile was the prevailing phase in the ZnS/$TiO_2$-1 sample.



a

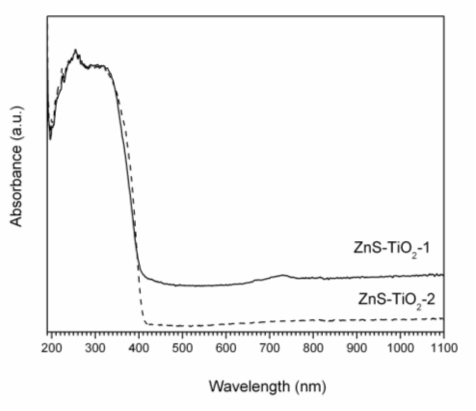


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**Fig. 2.** UV-vis absorbance spectrum of: a) $TiO_2$ P25 Degussa; b) mechanochemically synthesized ZnS/$TiO_2$ composites.

All the lines characteristic of $TiO_2$ P 25 were present in the diffraction pattern of the sample ZnS/$TiO_2$-2, which was prepared by wet mechanochemical synthesis of ZnS from zinc acetate and sodium sulfide on the surface of $TiO_2$ P 25. Partial transformation of the anatase into rutile was registered in this case. The specific surface area of the sample ZnS/$TiO_2$-1 was measured to be 36 $m^2g^{-1}$. The sample ZnS/$TiO_2$-2 had specific surface area 48 $m^2g^{-1}$ near to that of initial $TiO_2$ P25 (50 $m^2g^{-1}$). The sample ZnS/$TiO_2$-1 represents a less crystalline material, in comparison with the sample ZnS/$TiO_2$-2 (Fig. 1). The wide diffraction lines of the mechanochemically synthesized ZnS clearly prove the nano-sized nature of the sample [18]. The impact of the energy during the milling process is manifested in the form of phase transformation [19].

The diffuse-reflectance spectra (DRS) in the ultra-violet and in the visible range were recorded aiming at the investigation of the optical properties of the mechanochemically prepared ZnS/$TiO_2$ composites. The $TiO_2$ P25 Degussa has a wide absorption band in the range from 200 to 380 nm (Fig. 2a). For the mechanochemically synthesized ZnS/$TiO_2$ composites, an absorption edge is red shifted and the absorption tail is extended to 420 nm as shown in Fig. 2b.

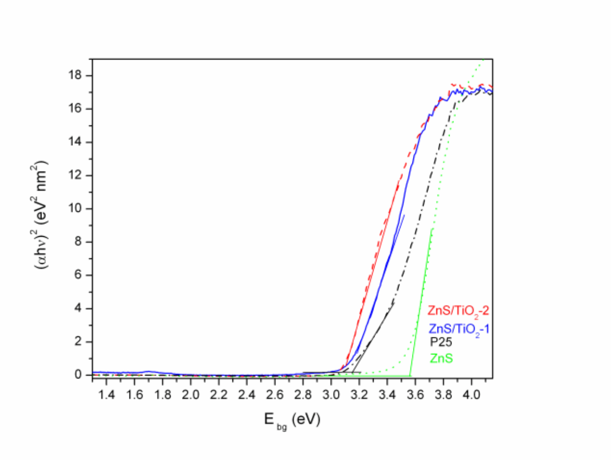
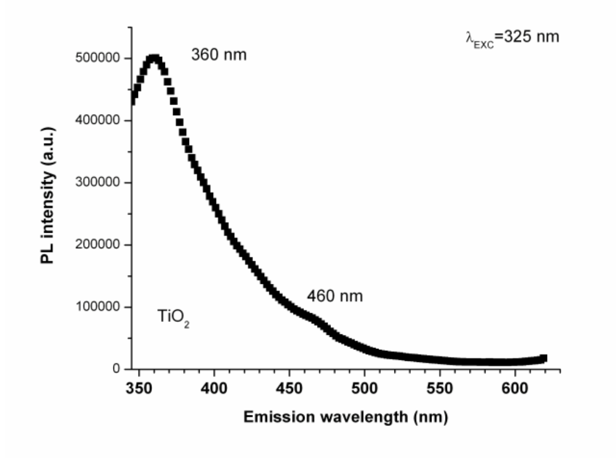


**Fig. 3.** Band gap energy $E_{bg}$ of $TiO_2$ P25 Degussa, and mechanochemically synthesized ZnS, ZnS/$TiO_2$-1 and ZnS/$TiO_2$-2 samples.

The method of UV-vis diffuse reflectance spectroscopy was employed to estimate the band gap energies of the prepared ZnS/$TiO_2$ composites. The minimum wavelength is required to promote an electrons depended upon the band gap energy $E_{bg}$ of the samples and it is given by relationship $E_{bg}=1240/\lambda$, where $\lambda$ is the wavelength in nanometers [20]. The band gap values were calculated using the UV-vis spectra from the following equation**:** $\alpha(h\nu) = A(h\nu-E_{bg})^{½}$ , where $\alpha$ is the absorption coefficient and $h\nu$ is the photon energy. The band gap energy is calculated by extrapolating a straight line to the abscissa axis. The value of $h\nu$ extrapolated to $\alpha=0$ gives an absorption energy, which corresponds to a band gap energy. The initial $TiO_2$ P 25 Degussa has $E_{bg}$=3.20 eV. The preliminary mechanochemically synthesized ZnS has a wider energy band gap $E_{bg}$=3.57 eV (Fig. 3). The estimated $E_{bg}$ value was 3.13 eV for ZnS/$TiO_2$ -1 sample and 3.08 eV for the ZnS/$TiO_2$-2 composite sample. These results suggest the possibility of application of these ZnS/$TiO_2$ composite materials as photocatalysts on degradation process with lower energetic requirements than $TiO_2$.



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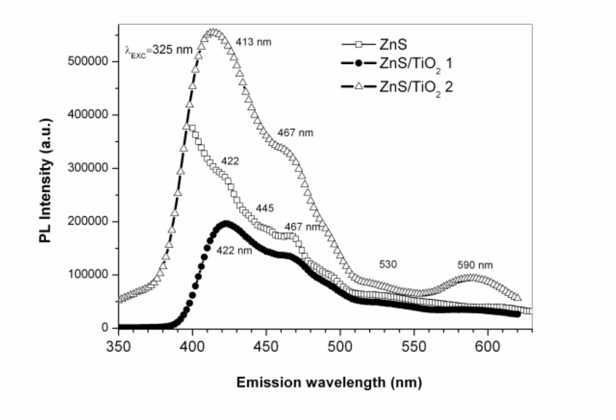

b

**Fig. 4.** Photoluminescence spectrum of: a) $TiO_2$ P25 Degussa; b) mechanochemically synthesized samples ZnS, ZnS/$TiO_2$-1 and ZnS/$TiO_2$-2.

The photoluminescence (PL) spectra of the mechanochemically synthesized ZnS, ZnS/$TiO_2$-1 and ZnS/$TiO_2$-2 samples were recorded in order to observe their emission behavior. All samples were photoexcited at wavelength 325 nm at room temperature. The PL spectrum of the initial $TiO_2$ P 25 Degussa is represented in Fig. 4a. The emission intensive peak in the spectrum of $TiO_2$ P 25 Degussa with a maximum in the near ultraviolet region at about 360 nm (Fig. 4a) can be ascribed to emission of a photon having energy equal or slightly higher than the band gap width of the anatase phase of $TiO_2$ and it gives evidence for a direct recombination of a photoexcited electron and a positively charged hole [21, 22]. As can be seen from Fig. 4b, the cubic ZnS phase is luminescence active. There are emission peaks at 422, 465, 496 and 590 nm. These emission peaks were also registered in the PL spectra of the mechanochemically prepared ZnS/$TiO_2$ composites. Wang et al. [23] reported the multiple defects related emission of ZnS. The emission intensity is decreased in the PL spectrum of ZnS/$TiO_2$-1 composite. The broad emission spectra of ZnS/$TiO_2$ composites are mainly located in the blue region. With its maximum intensity centered at 422 nm, which could be ascribed to the sulfur vacancy and defects in the ZnS microcrystals [28]. The blue shift of the first PL band from 422 to 413 nm in the PL spectrum of ZnS/$TiO_2$-2 composite was registered. The PL intensity of ZnS/$TiO_2$-2 is higher than ZnS/$TiO_2$-1. This is related to the presence of anatase phase in ZnS/$TiO_2$-2 sample provided with XRD (see Fig. 1). The emission peak observed at 465 nm could be associated with an interstitial zinc lattice defect. The emission peak at 496 nm is from the sulfur vacancy related emission [25]. The green PL emission peak at 590 nm can be associated with elemental sulfur species [26]. The photoluminescence emission is the result of two effects: part of the illuminating photons energy goes for non-radiative transition (transition between two energy levels of vibration of the modes of the crystal lattice). The other part is emitted as a result of recombination of photoexcited electrons and holes (photons of lower energy).

The photocatalytic activities of the mechanochemically synthesized ZnS/$TiO_2$ composites were evaluated by the degradation of representative industrial dye Methyl Orange (MO) in aqueous solution under UV irradiation. All experiments were performed under nature pH condition and room temperature. For comparison, the activities of ZnS and $TiO_2$ P25 Degussa were also investigated under the same conditions. The temporal changes in the concentration of MO were monitored by examining the variation in maximal absorption in UV-vis at 464 nm. In region, where Lamber-Beer law ($A=\varepsilon*c*l$) is significant the concentration of MO dye is proportional to absorbance, where $A$ is the absorbance, $c$ is the concentration of absorbing compound MO, $l$ is the length of absorbing layer and $\varepsilon$ is the molar absorbing coefficient. Fig. 5 shows the photocatalytic efficiencies ($C/C_o$) in presence of mechanochemically prepared ZnS and ZnS/$TiO_2$ composite materials. The $C_o$ is the initial concentration after achieve absorption/desorption equilibrium. On the basis of blank experiment, the self-photolysis of MO could be neglected (Fig. 5-curve 5). $TiO_2$ P25 Degussa was taken as reference for comparison purpose and in this case the MO degradation was about 70 % after 60 min. The photodegradation performance of MO can be ranked by decreasing order of activity as follows: $ZnS/TiO_2$-2 > $ZnS/TiO_2$-1 > $TiO_2$>ZnS.

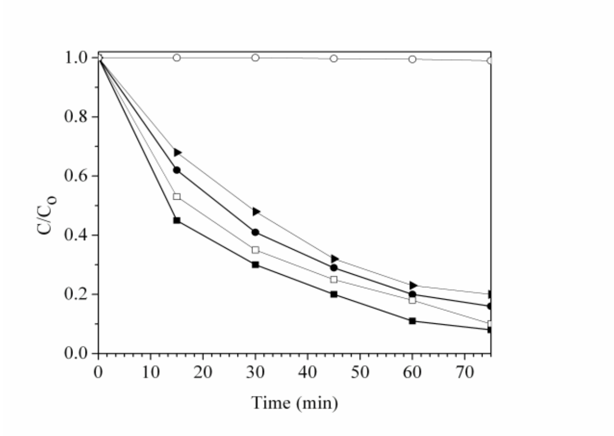

**Fig. 5.** Photodegradation effect of MO as a function of irradiation time of commercial $TiO_2$ P25 Degussa (●), and mechanochemically synthesized samples ZnS (▶), $ZnS/TiO_2$-1(□), $ZnS/TiO_2$-2 (■) and blank experiment (○).

In addition, after the degradation, reaction is completed; the $ZnS/TiO_2$-1 composite photocatalyst was separated centrifugally from the dye solution. Without further treatment, the recycled $ZnS/TiO_2$-1 composite was used to degrade the dye solution for the second time. The degradation rate remains almost unchanged, which shows that the $ZnS/TiO_2$-1 composite photocatalyst has also good repeatability.

## CONCLUSIONS

The present paper represents a detailed study of the structural, optical and photocatalytic properties of mechanochemically synthesized $ZnS/TiO_2$ composite materials. The XRD analysis of the $ZnS/TiO_2$-1 sample, prepared by dry milling in a planetary ball mill shows that in this case almost the full phase transition of anatase into rutile is occurred. However, the phase composition of $TiO_2$ P25 during the wet mechanochemical synthesis of the $ZnS/TiO_2$-2 composite sample is preserved. The specific surface area of this sample is close to the initial $TiO_2$ P25. DRS study reveals that all the mechanochemically synthesized samples show strong absorbance in the visible light region. The evaluated band gap values of the samples are 3.3, 3.57, 3.13 and 3.06 eV for $TiO_2$ P25, ZnS, $ZnS/TiO_2$-1 and for $ZnS/TiO_2$-2, respectively. The enhanced photocatalytic activity of decoloration of MO in aqueous solutions of the synthesized composite materials in the visible range of the spectrum is owing to the efficient separation of photoexcited electrons and holes – the charge carriers between the ZnS and the $TiO_2$ attached phases.

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## REFERENCES

1. A. Fujishima, T. N. Rao, D.A. Tryk, *J. Photochem. Photobiol. C. Photochem. Rev.*, **1**, 1 (2000).
2. M. Hoffmannn, S. Martin, W. Choi, D. Bahnemann, *Chem. Rev*., **95,** 69 (1995).
3. H. Tada, A. Hattori, Y. Tokihisa, K. Imai, N. Tohge, S. Ito, *J. Phys. Chem.* B, **104,** 4585 (2000).
4. S. Ummartyotin, Y. Infahsaeng, *Renewable and Sustainable Energy Rev.*, **55**, 17 (2016).
5. N. Jothi, A. Joshi, R. Vijay, A. Muthuvivayaagam, P. Sagayaraj, *Mater. Chem. Phys*., **138**, 186 (2013).
6. I. Bu, *J. Lumines*., **134**, 423 (2013).
7. Y. Choi, S. Lee, S. Kim, Y. Kim, D. Cho, M. Khan, Y. Sohn, *J. Alloy. Comp*., **675**, 46 (2016).
8. P. Baláž, E. Boldižárová, E. Godočíková, J. Briančin, *Mat. Lett.*, **57**, 1585 (2003).
9. P. Baláž, M. Achimovičová, M. Baláž, P. Billik, Z. Cherkezova-Zheleva, J.M. Craido, F. Delogu, E. Dutková, E. Gaffet, F.J. Gotor, R. Kumar, I. Mitov, T. Rojac, M. Senna, A. Streletskii, K. Wieczorek-Ciurowa, *Chem. Soc. Rev*., **42**, 7571 (2013).
10. C. Xu, S. De, A. Balu, M. Ojeda, R. Luque, *Chem. Commun*., **51**, 6698 (2015).
11. L. Takacs, M. Susol, *J. Solid State Chem*., **121**, 394 (1996).
12. A. Roy, G. De, *J. Photochem. Photobiol.* A Chemistry, **157,** 87 (2003).
13. N. Uzar, S. Okur, M.C. Aricom, *Sensor. Actuator. Phys*., **167**, 188 (2011).
14. P. Balaz, M. Balaz, E. Dutkova, A. Zorkovska, J. Kovac, P. Hronec, J. Kovac Jr, M. Caplovicova, J. Mojzis, G. Mojzisova, A. Eliyas, N.G. Kostova, *Mater. Sci. Eng. C,* **58**, 1016 (2016).
15. Z. Orel, M. Gunde, B. Orel, *Prog. Org. Coat.,* **30**, 59 (1997).
16. N.G. Kostova, M. Achimovičová, A. Eliyas, N. Velinov, P. Baláž, *Nanosci. and Nanotechnol.*, **12**, 52 (2012).
17. J. Niu, W. Xu, H. Shen, S. Li, H. Wang, L. Li, *Bull. Kor. Chem. Soc*., **33**, 393 (2012).

18. V. Sepelak, A. Duvel, M. Wilkeming, K.D., Becker, P. Heitjans, *Chem. Soc. Rev*., **42**, 7507 (2013).
19. I. Lin, S. Nadiv, *Mater. Sci. Eng*., **39**, 93 (1979).
20. K. Reddy, S. Panorama, A. Reddy, *Mater. Chem. Phys*., **78**, 239 (2002).
21. S. Liu, X-J. Zhao, Q. Zhao, X. He, J. Feng, *J. Electron Spectrosc. Relat. Phenom.*, **148**, 158 (2005).
22. D. Dastan, P. Loundhe, N. Chaure, *J. Mater. Sci.-Mater. Electr.*, **25**, 3473 (2014).
23. X. Wang, J. Shi, Z. Feng , M.Li, C. Li, *Phys. Chem. Chem. Phys.*, **13**, 4715 (2011).
24. P. Hu, Y. Liu, L. Fu, L. Cao, D. Zhu, *J. Phys. Chem. B*, **108**, 936-938 (2009).
25. A. Kole, C. Tiwary, P. Kumbhakar, *J. Mater. Chem*., C **2**, 4338 (2014).
26. A. Ye, X. Fang, G.Li, L. Zhang, *Appl. Phys. Lett.*, **85** 035 (2004).

# МЕХАНОХИМИЧЕН СИНТЕЗ И СВОЙСТВА НА $ZnS/TiO_2$ КОМПОЗИТИ

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(Резюме)

$ZnS/TiO_2$ композити бяха получени чрез твърдотелен механохимичен подход. Един $ZnS/TiO_2$ композитен материал беше получен в планетарна топкова мелница чрез сухо смилане на $TiO_2$ P 25 Degussa с предварително механохимично синтезиран ZnS с кубична структура от сфалеритав тип JCPDS 00-05-0566. Друг образец беше получен чрез мокър механохимичен синтез от цинков ацетат и натриев сулфид в присъствие на $TiO_2$ P 25 Degussa. Фазата и структурните промени бяха изследвани с помощта на РФА. Беше установено, че сухото смилане на смес от $TiO_2$ P 25 and ZnS индуцира пълно преобразуване на анатаза, присъстващ в $TiO_2$ P 25 Degussa, в рутил. Анатаз беше идентифициран в дифрактограмата на механохимично синтезирания образец чрез мокър метод. Дифузноотражателна спектроскопия беше приложена за определяне на енергията на забранената зона на механохимичносинтезираните образци. Фотокаталитичните свойства на получените $ZnS/TiO_2$ образци бяха изследвани във фотокаталитичното обезцветяване на багрило метил оранж като моделен замърсител във воден разтвор. За определяне на емисионното поведение на механохимично синтезираните $ZnS/TiO_2$ композитни материали бяха записани техните фотолуминесцентни спектри при стайна температура след възбуждане на образците с възбуждаща дължина на вълната 325 нм. Бяха наблюдавани сложни емисионни пикове. По-ниският интензитет на ивиците в спектра на образеца синтезиран чрез сухо механично стриване свидетелства за по-ниска скорост на рекомбиниране на фотовъзбудените електрони и дупки.