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Mineralization of pharmaceutical drugs by ZnO photocatalysts under UV light illumination

N. Kaneva*, A. Bojinova, K. Papazova, D. Dimitrov

Laboratory of Nanoparticle Science and Technology, Department of General and Inorganic Chemistry, Faculty of Chemistry and Pharmacy, University of Sofia, 1164 Sofia, Bulgaria

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Zinc oxide films were obtained by simple suspension method through mixing commercial ZnO powder, ethanol, and polyethylene glycol. Samples were deposited with one and five layers by dip coating. Film efficiency was evaluated by decolourisation of the pharmaceutical drugs Paracetamol and Chloramphenicol. Drugs mineralisation kinetics in distilled water upon UV light illumination was studied as a model system for contaminated wastewater. Photocatalytic experiments with commercial ZnO powders (unannealed and annealed) were also investigated. The films and the powders were characterised by SEM, XRD, BET, and UV-vis spectroscopy. The effects of catalysts amount and annealing temperature were examined. ZnO showed higher photocatalytic efficiency in Paracetamol degradation as compared to that of Chloramphenicol.

Key words: ZnO, thin films, powders, photocatalysis, pharmaceutical drugs.

INTRODUCTION

Zinc oxide is one of the most important inorganic, multifunctional, and promising materials in the family of wide-gap semiconductors due to its unique properties, such as chemical, radiation and thermal resistance, optical transparency, and high piezoelectric and photocatalytic properties. It has been extensively used in industrial and medical applications such as UV light emitting diodes [1], UV laser [2], solar cells [3], gas sensors [4], photocatalysts [5], photovoltaic devices [6], toxicological materials [7], etc. It is well known that the properties of nanomaterials depend not only on the composition but also on the structure. There are various ZnO nanostructures, such as nanoparticles [8], nanorods [9], nanoflowers [10], nanowires [11], and nanosheets [12], which have been successfully synthesised by different approaches: thermal decomposition [13,14], sol-gel method [15], microwave method [16], chemical precipitation method [17], hydrothermal method [18], etc.

ZnO is widely utilised semiconductor catalyst that exhibits an attractive and promising property. In regarding to its high photocatalytic activity, ZnO nanostructures have attracted a considerable attention, which is due to their superior performance in the range of ultraviolet and visible light compared with well-known catalysts such as titania [19]. Zinc oxide nanomaterials exhibit unique properties owing to their complicated structure, among which photocatalysis is the most important for degradation of organic pollutants in aqueous solution: dyes [20,21], pesticides [22], pharmaceutical drugs [23–25], etc.

Pharmaceutical products are considered harmful pollutants in the aquatic ecosystem even at low concentrations due to their continuous input and accumulation in the environment. They have been detected worldwide in environmental matrices indicating their ineffective removal from wastewaters using conventional purification methods. To prevent this contamination several processes of drug removal have been studied [26]. Heterogeneous photocatalysis of organic pollutants in wastewater is an advanced method for environmental protection. As a well-known photocatalyst, ZnO has the potential for degradation and complete mineralisation of environmental pollutants [27]. Besides photopurification of water suspensions seems more promising (high scores and degree of photodegradation and a greater amount of treated solution), there are crucial limitations for its application in practice: unsolved problems like light penetration into solutions and final separation of the catalysts from treated solution. Therefore, the purification of contaminated water *via* photocatalytic films is still preferable for practical application.

In this study, nanostructured ZnO photocatalysts (powders and thin films, prepared by dip coating from suspensions) were characterised and tested for the photocatalytic degradation of two commonly used drugs: Paracetamol (PCA) and Chloramphenicol (CA). Photomineralisation kinetics of drugs in

* To whom all correspondence should be sent
E-mail: nina_k@abv.bg

water upon UV light illumination was studied as a model system for purification of contaminated pharmaceutical wastewater.

EXPERIMENTAL

Reagents and materials

Commercial zinc oxide powder and absolute ethanol (>99.0%) were supplied from Fluka. Polyethylene glycol (PEG 4000) was kindly provided from the Institute of Pure Compounds (University of Sofia, Bulgaria). Glass slides (ca. 76 mm×26 mm), used for substrates of ZnO films, were delivered by ISO-LAB (Germany). Distilled water was used for all experiments.

Paracetamol ($C_8H_9NO_2$, λ_{max} = 243 nm, ≥99.0% purity, Actavis) and Chloramphenicol ($C_{11}H_{12}Cl_2N_2O_5$, λ_{max} = 278 nm, ≥99.0% purity, Actavis) were used as model contaminants in the photocatalytic activity experiments. The former drug belongs to a group of medicines known as analgesics or painkillers. It is used to relieve mild-to-moderate fever, headache, migraine, toothache, muscle pain, or early stages of flu. It is also useful for lowering a raised temperature, such as after childhood immunisation. In combination with other drugs, it enhances pharmacological and side effects. The latter pharmaceutical product is an antibiotic useful for the treatment of a number of bacterial infections. Chloramphenicol is a broad spectrum antibiotic with antibacterial and bacteriostatic type of action against Gram positive and Gram-negative bacteria. It is applied only to treat or prevent simple infections (e.g. cold, flu, throat infections), if safer and effective medicines can be used. The side effects of both pharmaceutical drugs are shown in Table 1.

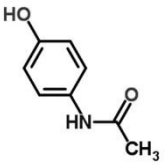
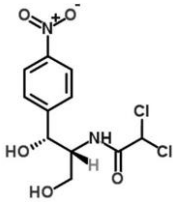
Preparation and characterization of ZnO powder photocatalysts

The commercial ZnO powder (Fluka) to be tested as a photocatalyst was annealed for 1 h at 500 °C. To prepare the respective thin films polyethyleneglycol (PEG-4000) was dissolved in absolute ethanol upon constant stirring and then heated for 30 min at 70 °C until a homogenous solution was formed. Pure (unannealed) ZnO powder was dispersed in ethanol (60 ml) and mixed with the PEG-4000 solution. The obtained suspension was stirred for 10 min and sonicated (15 kHz) for additional 30 min. To prepare the films, glass substrates were dipped in the suspension and withdrawn at a rate of 0.9 cm/min at room temperature [28]. Films with different number of coatings (one and five) were manufactured. The films were dried at 80 °C for 30 min after each coating. The dried films were annealed at 500 °C for 1 h in order to decompose the organics and to get the final ZnO films for photocatalytic tests. The photocatalyst samples were characterised by means of SEM (JSM-5510 JEOL), XRD (Siemens D500 with CuKα radiation within 2θ range of 10−80 deg at a 0.05-deg step and counting time of 2 s/step), BET analysis before and after annealing (N_2 adsorption), and UV-vis spectroscopy (Evolution 300 Thermo Scientific).

Photocatalytic procedure

The photocatalytic tests [29] were carried out in cylindrical glass reactors of 250-ml and 150-ml volume for powders and films, respectively, equipped with magnetic stirrer and UV lamp (maximum emission at 370 nm) and placed at 10 cm above the purified solution. Light power density at the sample position measured with a research radiometer (Ealing Electro-optics) was 0.66 mW/cm^2. PCA and CA photodegradation was monitored by UV-vis absorbance spectroscopy after aliquot sampling at regular time intervals. Each sample was turned back to the reaction mixture after spectrophotometrical measurement. All photocatalytic experiments were performed at a constant stirring rate of 500 rpm at room temperature (23 ± 2°C). The initial concentrations of pollutants were as follows: (i) 50 and 25 ppm (PCA and CA) in case of powder photocatalysts, and (ii) 15 and 8 ppm (PCA and CA) in case of films.

Table 1. Side effects of Paracetamol and Chloramphenicol.

Drugs	Formula	Side effects
Paracetamol		• high doses: hepatotoxicity, skin, liver, and kidney damage; • prolonged use: changes the effect of other pharmaceutical drugs (Rifampicin, Cimetidine, Chloramphenicol, Busulfan).
Chloramphenicol		• high doses: violation of blood-forming apparatus; haemolytic anemia leukemia, nausea, vomiting, diarrhea, stomatitis (gastrointestinal) reactions, headache, depression (neurotoxic effects), rash, itching, burning, redness, swelling, fever (allergic); • Prolonged use: development of fungal infections and resistance of microorganisms to the product.

RESULTS AND DISCUSSION

Characterisation of ZnO photocatalysts

The morphology, composition, and structure of the commercial ZnO powder (unannealed and annealed at 500 °C) were examined by scanning electron microscopy (Fig. 1 a, b). The SEM images show particles of various sizes and shape. Sintering (densification) of the ZnO particles and an increased share of large agglomerates in the range of 0.4–0.6 μm were observed in the case of annealing.

The SEM investigation indicated that the ZnO films had a homogenous morphology (Fig. 1 c, d). The film surface is uniform and porous. After annealing, the layer did not peel off. This is due to the PEG, which acts as a stabiliser. Higher magnification revealed a fine granular structure of the film morphology. No significant difference in the morphology of films prepared with different number of coatings could be observed. However, the films obtained by five coatings were thicker (4 μm) then those obtained by one coating (2 μm).

Phase analysis and crystallinity of the prepared ZnO powder samples, unannealed and annealed at 500 °C, and ZnO thin films, with one or five layers, were determined by XRD analysis (Fig. 2).

All diffraction peaks can be indexed to a hexagonal structure of ZnO, in agreement with the literature data. No characteristic peaks of any impurities are observed. The three characteristic peaks ((left to right) (100) - $2\theta = 31.76°$; (002) - $2\theta = 34.39°$; and (101) - $2\theta = 35.67°$) correspond to the different crystallographic orientations of the crystal lattice of ZnO wurtzite. They are narrow with high intensity, which indicate that the ZnO nanostructures have high crystallinity. The crystallite size of the commercial ZnO powder was 30 nm as calculated by the Scherer equation. The XRD spectrum of annealed ZnO powder shows that annealing caused an increase of the crystallite sizes from 30 to 100 nm. The results of X-ray diffraction were confirmed by BET analysis. The specific surface area of unannealed powder was lower (9.1 m^2/g) compared to annealed zinc oxide (10.3 m^2/g). This parameter affected the photocatalytic efficiency for degradation of pharmaceutical drugs.

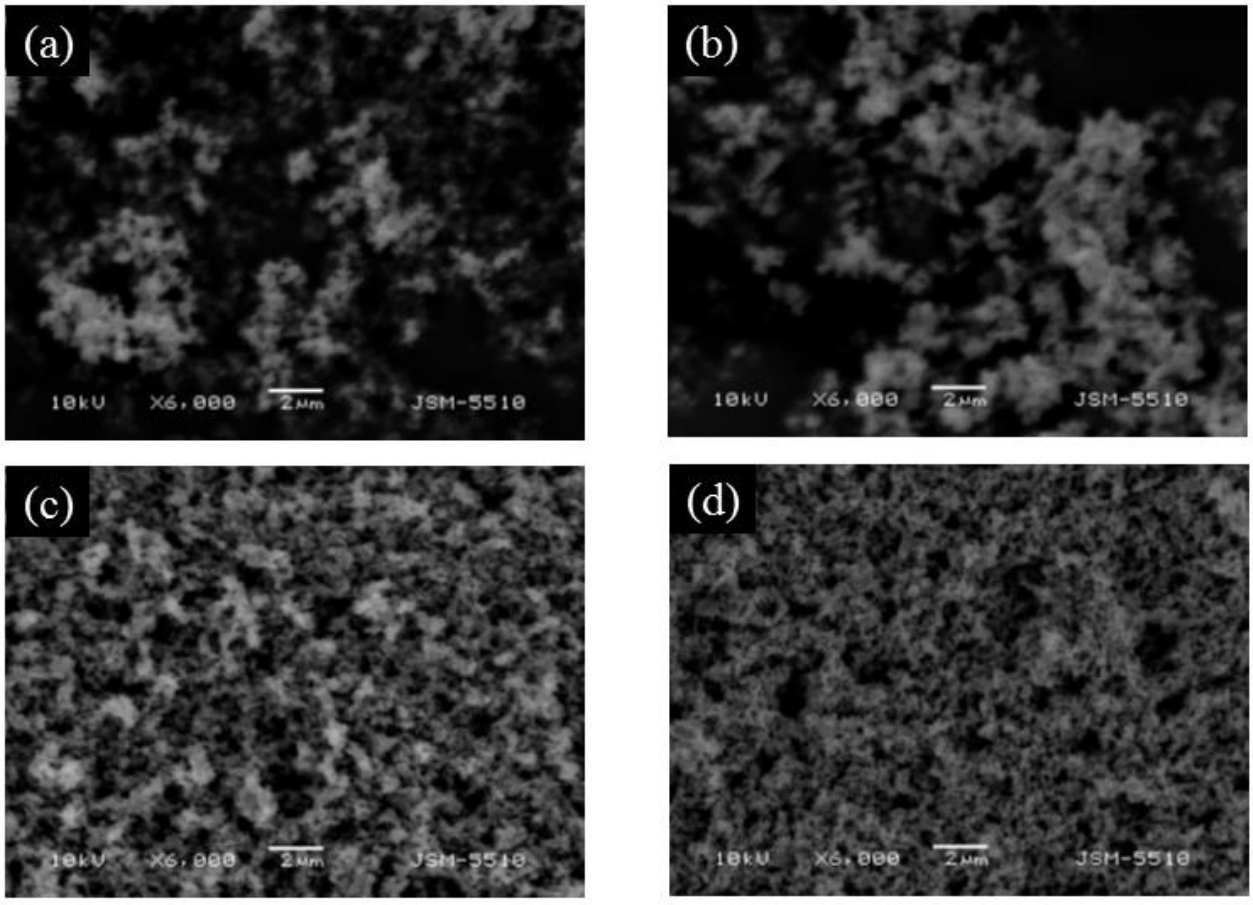


Fig. 1. SEM images: (a) unannealed ZnO powder, (b) annealed ZnO powder, (c) ZnO film with one coat, and (d) ZnO film with five coats.

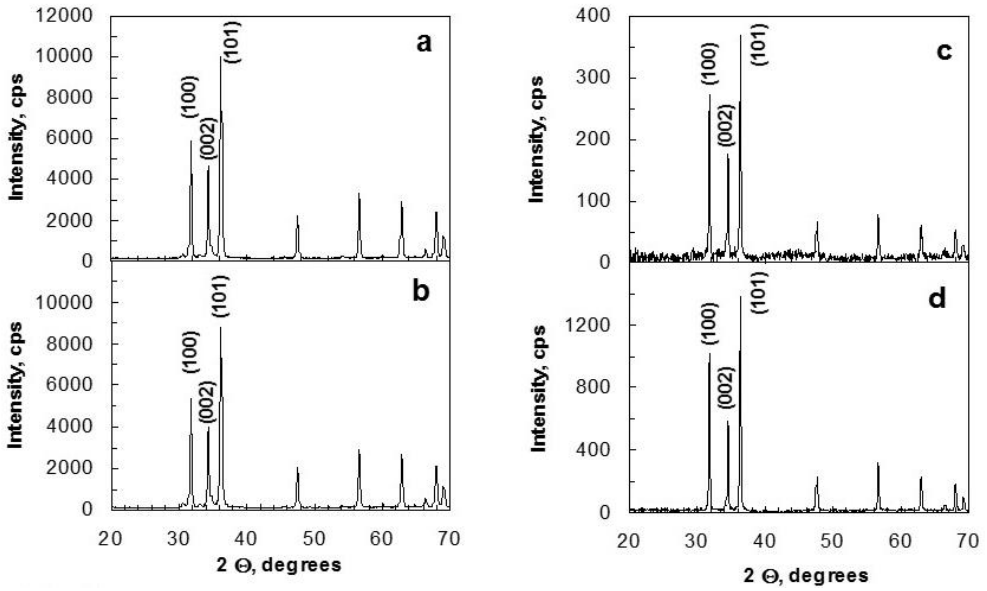


Fig. 2. XRD spectra of: (a) non-annealed ZnO powder, (b) annealed ZnO powder; (c) ZnO film with one coat; (d) ZnO film with five coats.

Degradation of pharmaceutical drugs by ZnO photocatalysts

In our research, Paracetamol and Chloramphenicol are used as model contaminants in the catalytic experiments. Figure 3 displays the PCA and CA degradation kinetics in aqueous solution using ZnO powders and UV light illumination. Annealing influences crystallinity degree, particle size, surface morphology, and therefore, the photocatalytic efficiency of the ZnO nanoparticles. As seen, the annealed powders demonstrate higher efficiency, 96.67% (PCA) and 80.86% (CA) for two hours, in comparison with unannealed ZnO: 90.40% (PCA) and 72.51% (CA) for two hours. The photocatalytic results are in good agreement with calculated values of the rate constants *k*.

Changes in the mineralisation degree of the pharmaceutical pollutants during photocatalysis for 240 min are presented in Fig. 4. As seen the intensity of the main peaks smoothly decreased with illumination time without any formation of new peaks due to intermediates or by-products. The latter confirms complete mineralisation of the drugs by annealed ZnO powders.

The relationship between drug degradation and irradiation time (240 min) is illustrated in Fig. 5. It is evident that the light-induced mineralisation activity increases upon increasing powder film thickness.

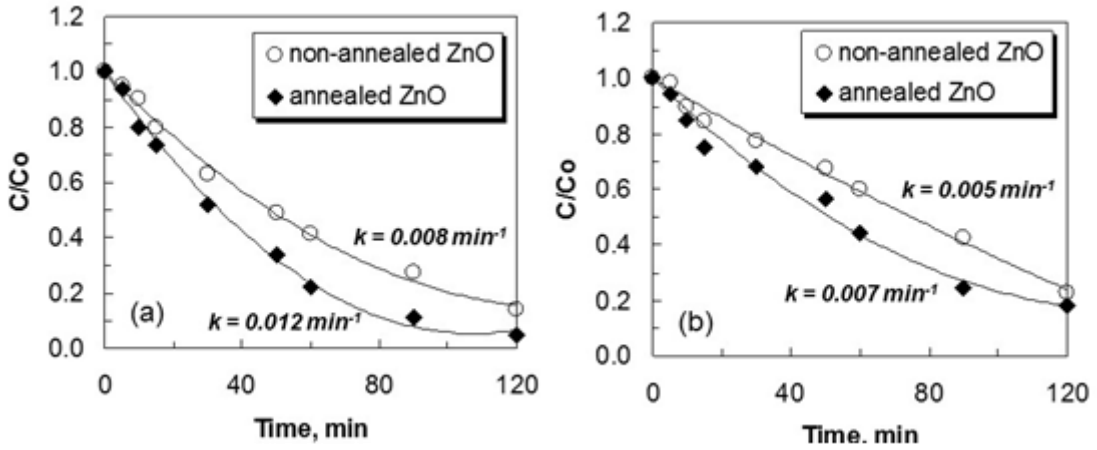


Fig. 3. Decrease in (a) Paracetamol and (b) Chloramphenicol concentration versus time upon UV light illumination with annealed and unannealed ZnO powders.

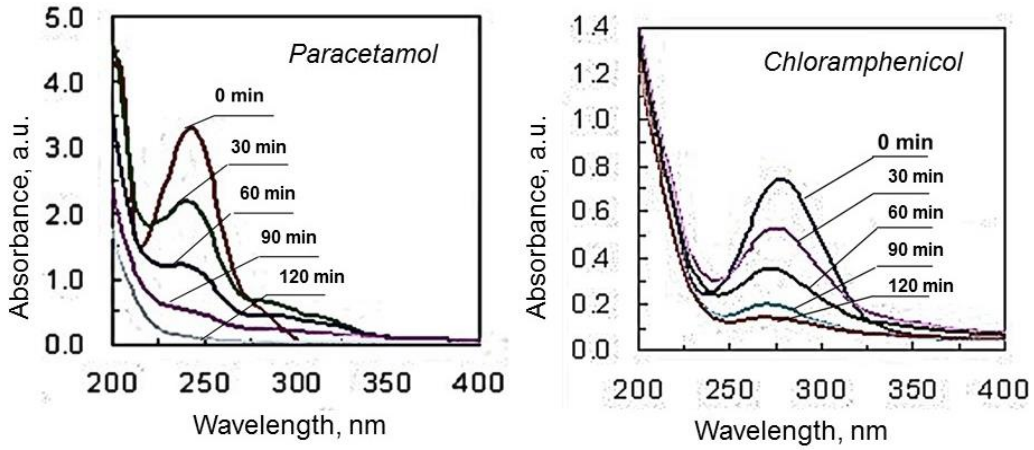


Fig. 4. Mineralisation of Paracetamol (50 ppm) and Chloramphenicol (25 ppm) with photocatalysis time.

The reason for this effect is a larger amount of zinc oxide deposited on the glass substrate. Nanostructure films manifested a higher degradation percentage of Paracetamol (D_{5coats} = 81.15% for 4 h) compared to Chloramphenicol (D_{5coats} = 68.48% for 4 h) under UV light illumination.

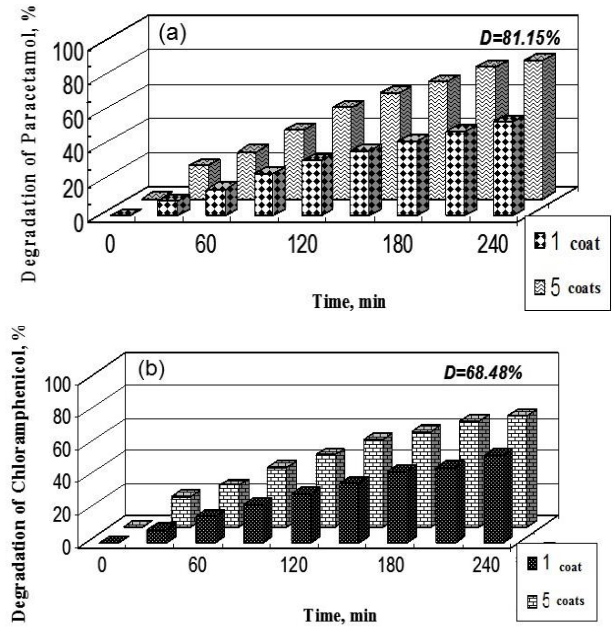


Fig. 5. Paracetamol (a) and Chloramphenicol (b) bleaching kinetics by ZnO films with one and five coats.

A faster mineralisation of Paracetamol by ZnO photocatalysts in comparison with that of Chloramphenicol is related to different drug molecule structures (Table 1) and degradation pathways. PCA photodegradation is a result of successive hydroxylation at the benzene ring moiety of paracetamol, which finally leads to its rupture. The process is initiated by highly reactive hydroxyl radicals formed after irradiation of ZnO and includes a number of products: hydroquinone, monohydroxy paracetamol, dihydroxy paracetamol, and aliphatic carboxylic acids (fumaric and malic) at the end [30]. CA photodecomposition is a more complicated process of two stages: dechlorination and denitrification [31]. According to the literature the nitro group in nitroaromatics can easily be eliminated *via* electrophilic substitution of the •OH radicals at the *para* position in the aromatic ring. Then the NO_2^- group can be oxidised to NO_3^-. Chloramphenicol can undergo also a reductive degradation pathway. Before forming nitrate ions, the nitro group may be reduced to an amine group on the ring and then released as ammonia.

CONCLUSIONS

This work demonstrates a simple dip-coating method for synthesis of zinc oxide powder films with one or five layers from suspension. The films and the respective powders were characterised by scanning electron microscopy, X-ray diffraction, and specific surface area measurements. SEM images showed that the films were composed of compact and dense layers. The powder films expressed a granular morphology without any crack. XRD results revealed that all powders and films were of hexagonal wurtzite structure of ZnO. The crystallite size of the zinc oxide powders increased with annealing temperature. BET analysis confirmed these results. Photocatalytic reaction kinetics was systematically studied for degradation of pharmaceutical drugs under UV light illumination. The ZnO photocatalysts mineralised Paracetamol faster in comparison with the antibiotic. Thin films prepared by five layers from suspension exhibited a higher efficiency than those prepared by one layer.

The photocatalytic activity of the powders was enhanced with annealing temperature.

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REFERENCES

1. Ch. Huang, J. Lai, *Org. Electron.*, **32**, 244 (2016).
2. P. Shewale, Y. Yu, *Ceram. Int.*, **42**, 7125 (2016).
3. J. Tang, Z. Tseng, L. Chen, S. H. Chu, *Sol. Energ. Mat. Sol. C*, **154**, 18 (2016).
4. V. Galstyan, E. Comini, C. Baratto, G. Fagilia, G. Sberveglieri, *Ceram. Int.*, **41**, 14239 (2015).
5. Y. Weng, K. Hsiao, *Int. J. Hydrogen Energ.*, **40**, 3238 (2015).
6. A. Sharma, J. Franklin, B. Singh, G. Andersson, D. Lewis, *Org. Electron.*, **24**, 131 (2015).
7. R. Roy, M. Das, P. Dwivedi, *Mol. Immunol.*, **63**, 184 (2015).
8. K. Omri, I. Najeh, L. Elmir, *Ceram. Int.*, **42**, 8940 (2016).
9. C. Yilmaz, U. Unal, *Appl. Surf. Sci.*, **368**, 456 (2016).
10. A. Umar, H. Algarni, S. Kim, M. Al-Assiri, *Ceram. Int.*, **42**, 13215 (2016).
11. R. Bahramian, A. Moshaii, H. Eshghi, *Mater. Lett.*, **179**, 222 (2016).
12. J. Yang, Y. Wang, J. Kong, H. Jia, Z. Wang, *Opt. Mater.*, **46**, 179 (2015).
13. I. Kontopoulou, A. Angelopoulou, N. Bouropoulos, *Mater. Lett.*, **165**, 87 (2016).
14. N. Kaneva, A. Bojinova, K. Papazova, D. Dimitrov, *Catal. Today*, **252**, 113 (2015).
15. T. Demes, C. Ternon, D. Riasseto, H. Roussel, L. Rarenne, I. Gelard, C. Jimenez, V. Stambouli, M. Langlet, *J. Phys. Chem. Solids*, **95**, 43 (2016).
16. Q. Al-naser, J. Zhou, G. Liu, L. Wang, *Ceram. Int.*, **42**, 828 (2016).
17. R. Suntako, *Mater. Lett.*, **158**, 399 (2015).
18. Y. Sun, H. Guo, W. Zhang, T. Zhou, Y. Qiu, K. Xu, B. Zhang, H. Yang, *Ceram. Int.*, **42**, 9648 (2016) .
19. H. Maleki-Ghaleh, M. Shahzadeh, S. Hoseinizadeh, A. Arabi, E. Aghaie, M. SIladati, *Mater. Lett.*, **169**, 140 (2016).
20. H. Seo, H. Shin, *Mater. Lett.*, **159**, 265 (2015).
21. L. Saikia, D. Bhuyan, M. Saikia, B. Malakar, D. Dutta, P. Sengupta, *Appl. Catal. A: General*, **490**, 42 (2015).
22. S. Navarro, J. Fenoll, N. Vela, E. Ruiz, G. Navarro, *J. Hazard. Mater.*, **172**, 1303 (2009).
23. M. Shakir, M. Faraz, M. Sherwani, S. Al-Resayes, *J. Lumin.*, **176**, 159 (2016).
24. M. El-Kemary, H. El-Shamy, I. El-Mehasseb, *J. Lumin.*, **130**, 2327 (2010).
25. B. Peake, R. Braund, L. Tremblay, A. Tong, in: The Life-Cycle of Pharmaceuticals in the Environment, Elsevier Ltd., 2016, Ch. 6, pp. 153-202.
26. M. Klavarioti, D. Mantzavinos, D. Kassinos, *Environ. Int.*, **35**, 402 (2009).
27. S. Rehman, R. Ullah, A. Butt, N. Gohar, *J. Hazard. Mater.*, **170**, 560 (2009).
28. C. Dushkin, S. Stoianov, A. Bojinova, S. Russev, *Ann. Univ. Sofia, Fac. Chimie*, **98-99**, 73 (2006).
29. N. Kaneva, I. Stambolova, V. Blaskov, Y. Dimitriev, A. Bojinova, C. Dushkin, *Surf. Coat. Tech.*, **207**, 5 (2012).
30. E. Moctezuma, E. Leyva, C. A. Aguilar, R. A. Luna, C. Montalvo, *J. Hazard. Mater.*, **243**, 130 (2012).
31. A. Chatzitakis, C. Berberidou, I. Paspaltsis, G. Kyriakou, T. Sklaviadis, I. Poulios, *Water Res.*, **42**, 386 (2008).

МИНЕРАЛИЗАЦИЯ НА ЛЕКАРСТВА С ФОТОКАТАЛИЗАТОР ZnO И УВ-ОБЛЪЧВАНЕ

Н. Канева*, А. Божинова, К. Папазова, Д. Димитров

Лаборатория „Наука и технология на наночастиците", катедра „Обща и неорганична химия", Факултет по химия и фармация, Софийски университет, бул. „Джеймс Баучер" 1, 1164 София, България

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(Резюме)

Получени са филми от цинков оксид чрез прост суспензионен метод – смес от търговски ZnO на прах, етанол и полиетилен гликол. Пробите са отложени с един и пет слоя, използвайки метода на потапяща се подложка. Ефективността на филмите е изследвана с разграждане на фармацевтичните лекарства – Парацетамол и Хлорамфеникол. Изследвана е кинетиката на минерализация на лекарствата в дестилирана вода в присъствие на УВ светлина като моделна система за пречистване на замърсени отпадъчни води. Проведени са и фотокаталитичните опити с търговски ZnO прахове (ненакалени и накалени). Филмите и праховете са охарактеризирани със СЕМ, рентгеноструктурен анализ, метода БЕТ и УВ-видима спектроскопия. Изследван е ефектът на количеството катализатор и температурата на накаляване. Цинковият оксид показва по-висока фотокаталитична ефективност при разграждане на Парацетамол в сравнение с Хлорамфеникол.