Bulgarian Chemical Communications, Volume 47, Number 1 (pp. 402–408) 2015

Sol aging effect on the structure and photocatalytic action of ZnO films for pharmaceutical drugs degradation

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

Received December, 2014; Revised January, 2015

In this work, ZnO thin films are prepared by sol–gel method and the effect of aging time of the ZnO sol on the structural and photocatalytic properties of the films is studied. ZnO sol is aged for different periods (0, 30 and 60 days). Nanocrystalline thin films with different thickness (one or five coats) are deposited on glass substrates via dip-coating technique. The structural properties of samples are analyzed by Scanning Electron Microscopy and X-ray diffractometer. The effect of aging time of the starting sol in respect to photocatalytic degradation of the pharmaceutical drugs (*Paracetamol* (*PCA*) and *Chloramphenicol* (*CA*)) is studied by UV-vis spectroscopy. The experiments are conducted under UV and visible light irradiation. The results show that the increased aging time of the starting ZnO solution generally promotes photocatalytic activity. The films with one coating have lower rate constants of degradation with comparison to the other samples. The thin films with five coats obtained from ZnO sol, aged 60 days exhibit highest photocatalytic degradation of the drugs (*PCA*: UV – 84.57% and Vis – 65.66%; *CA*: UV – 67.2% and Vis – 52.2%) in comparison to the freshly prepared ones (*PCA*: UV – 29.60% and Vis – 18.62 %; *CA*: UV – 18.43% and Vis – 14.12%).

Key words: ZnO sol-gel films, aging time, photocatalysis, UV-visible, pharmaceutical dugs.

INTRODUCTION

In the recent years the interest in wide band gap oxide semiconductor materials such as zinc oxide (ZnO) [1], indium oxide (In_2O_3) [2], tin oxide (SnO_2) [3] and titanium oxide (TiO_2) [4] has notably increased. These materials in form of thin film present transport and optical properties that make them good candidates for modern applications. ZnO is a well known, chemically stable material, commonly used as coating material in optical thin films and has been applied in many other fields [5–7]. ZnO has also received extensive attention due to its excellent photocatalytic properties [8–10]. By photocatalytic processes in polluted air and water, using of UV irradiated inorganic oxides, contaminants such as textile dyes, pesticides and pharmaceutical drugs have been degraded [11–14].

Although pharmaceuticals have been consumed for many decades, only during the last few years their fate and release in the aquatic environment have been recognized as one of the most urgent problems of environmental chemistry. Pharmaceutically active compounds such as analgesics, antibiotics, steroids, hormones, etc., have been detected in several public water systems in Europe, USA and Australia as a result of human, animal and plant activities [15, 16]. Mass balance of the input and output of pharmaceuticals in sewage treatment plants indicates that during sewage treatment not all pharmaceuticals are removed quantitatively [17] from the surface and underground water. Their environmental presence gains importance because they are related to abnormal physiological processes in reproduction, increased incidences of cancer, development of antibiotic-resistant bacteria and potential increased toxicity of chemical mixtures. Therefore, the photocatalytic decomposition of pharmaceutical products of environmental concern has been studied extensively and it has been demonstrated that heterogeneous photocatalysis using ZnO (nanowires, nanoparticles, thin films, etc.) as catalyst can be an alternative to conventional methods for their removal from water [13].

Different chemical and physical methods have been employed to prepare ZnO films including sputtering [18], chemical bath deposition [19],

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

pulsed laser deposition [20], sol–gel [10, 21, 22] and spray pyrolysis [23]. The chemical methods present advantages as low cost, safety and easy handling equipments. The sol–gel process is one of the most appropriate methods to prepare thin oxide coatings due to some advantages, such as depositions are with good homogeneity, low processing temperature, low equipment cost and good optical properties. The preparation conditions of ZnO thin films by sol–gel method can influence the physical properties of the film [16, 17].

In this work we report ZnO thin films deposited on glass substrates by sol–gel technique, using zinc acetate dehydrate as a starting reagent. The ZnO sol is aged for different period – 0, 30 and 60 days. The deposited films with dip-coating technique are characterized using SEM, XRD and UV–vis analysis. The effect of the aging time of the starting solution as well as the number of coatings (1 and 5 coatings) is investigated for the photocatalytic degradation of *Paracetamol* (PCA) and *Chloramphenicol* (CA). *Paracetamol* (*PCA*) and *Chloramphenicol* (*CA*) are common drugs used extensively in variety medical applications. Therefore, they are chosen as model pollutants to test the activity of ZnO films with different aging time of the starting solution.

EXPERIMENTAL

Precursor sol preparation

Zinc acetate dihydrate ($Zn(CH_3COO)_2 \bullet 2H_2O$, ≥99.5% purity, Fluka) was chosen as Zn precursor. The zinc compound was dissolved in a solution containing 2-methoxyethanol ($C_3H_8O_2$, ≥99.5% purity, Fluka) and monoethanolamine (MEA, $HOCH_2C_2NH_2$, ≥99.0% purity, Fluka) used as a solvent and stabilizer, respectively. The mixture was continuously stirred at room temperature until a clear and homogeneous solution was reached. The obtained solution was heated up at 60 °C upon magnetic stirring for 1 hour. The final solutions were kept at room temperature in darkness, in order to avoid some light-assisted reaction, and to limit the variables that may affect the solution. No visible changes were observed in the precursor when stored in darkness at room temperature for at least 2 months. An aliquot was taken each 0, 30 and 60 days for the films deposition.

ZnO films deposition and characterization

The thin films were deposited onto cleaned and dried glass substrates (ca. 76×26 mm, ISO-LAB Germany) by dip-coating technique. The films deposition consists in a dipping process of the substrate into the starting solution and then pulling out at a constant velocity at room temperature. It was experimentally found out that best film quality was obtained at rates of 0.9 cm/min. The dipping process can be repeated until the desirable number of coatings or immersions is reached. The film thickness can be controlled by the number of coating cycles. Films were deposited with one and five coats from sols aged for different times. After each dipping process, the films were thermally treated at 80 °C for 10 min, in order to remove the remaining solvents. The films were cooled at atmospheric conditions. As a final step, the films were subjected to another thermal treatment at 500 °C for 1 h, in order to synthesize the final compound (ZnO) for photocatalytic tests.

The surface morphology of the ZnO films obtained from sols of different aging times was characterized by Scanning Electron Microscope (SEM, JEOL JSM-5510). The crystallinity and size of crystallites were determined by X-Ray Diffraction (XRD) at room temperature by powder diffractometer (Siemens D500 with CuKα radiation within 2θ range 30–70 deg at a step of 0.05 deg 2θ and counting time 2 s/step). Drug concentrations in the aqueous solution after 4 h UV or visible irradiation and the optical absorbance spectra were measured by spectrophotometer Evaluation 3000 Thermo Science in the wavelength range from 200 to 600 nm.

Photocatalysis

The photocatalytic efficiency was measured in a glass reactor (250 ml), equipped with magnetic stirrer (rotating speed controlled by stroboscope), UV (maximum emission at 370 nm; the light power density at the sample position was 0.66 mW/cm^2 as measured with Research Radiometer of Ealing Electro-optics, Inc.). The distance between the glass reactor and UV lamp was 15 cm. The mineralization of pharmaceutical drugs was monitored by UV-vis absorbance spectroscopy after aliquot sampling at regular time intervals. The sample was fixed at 0.5 cm bellow the drugs solution surface. The mineralization has been calculated as:

$$D\% = \left[\frac{C_0 - C}{C_0}\right] \times 100 \qquad (1)$$

where C_0 is the initial concentration of drugs and C is the concentration of drugs after irradiation in selected time interval.

Experiments were carried out with six series of samples: nanostructured ZnO films obtained at different aging time of the starting solution (0, 30 and 60 days), prepared with 1 and 5 layers. The drugs solution volume was 150 mL. The initial concentra-

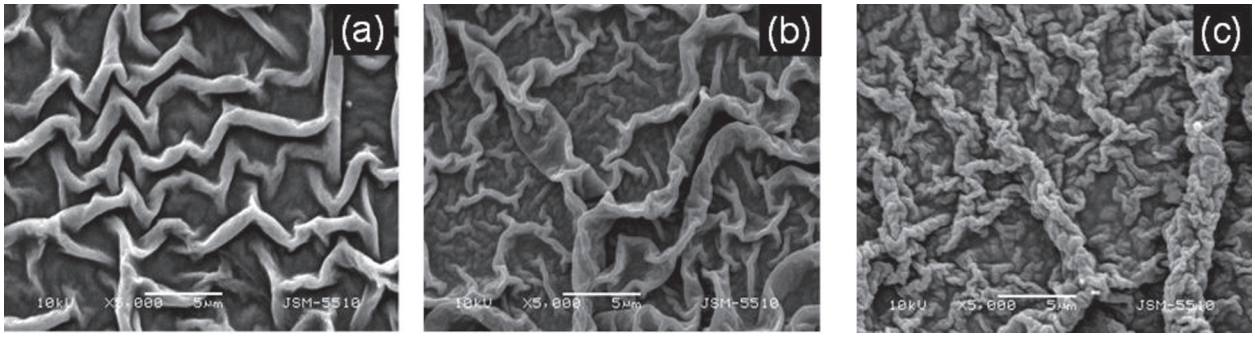

Fig. 1. SEM images of ZnO films with five coats obtained from sols aged (a) 0, (b) 30 and (c) 60 days

tion of PCA and CA was 20 ppm. All photocatalytic tests were performed at constant stirring rate (500 rpm) at room temperature (23±2 °C).

RESULTS AND DISCUSSION

Structure analysis of ZnO films

The SEM images of the surface of ZnO films deposited at different aging time with 5 coats are shown in Fig. 1. These micrographs clearly show that there are changes in the morphology of the thin films with the aging time. The surface on the nanostructure films (ZnO starting sol, stayed 0 day) is homogeneous with typical ganglia-like structure. Their shape, size and thickness are changed, depending of the aging time of the starting solution. The increase of aging time of ZnO sol increases the volume and size of ganglia-like hills (Fig. 1 b, c), which are looking more branched and developed at their ends. The sol-gel films, sol aged 60 days, are more uniform and show much better adhesion of the layers and the highest density of the film. In this case the inorganic polymer-oxide network is uniformly built up. The ganglia-like structure seems reproducible irrespective on the conditions of films deposition and annealing.

The XRD patterns of ZnO films at 0, 30 and 60 day aged solution with 5 coats are presented in Fig. 2. The wurtzite-like structured ZnO is registered as only crystalline phase. The samples obtained at 500 °C by 0, 30 day-aged solution (Fig. 2a, b) show more intensive diffraction peak (002) at 34.4^o which suggests a preferential orientation along the c-axis. But the films deposited by the starting solution with aging time 60 days are preferentially oriented along the (101) direction in turn (Fig. 2c). This result is similar to that reported by Guerra et al. [24] and Rozati et al. [25] describing ZnO thin films obtained by spray pyrolysis. The authors found that the aging time of the starting solution has a great effect on the

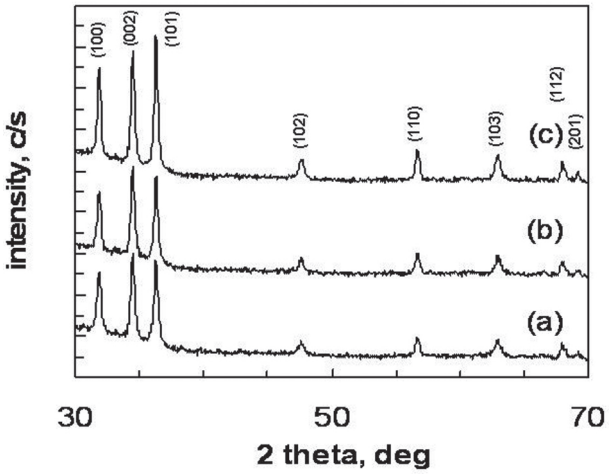

Fig. 2. XRD patterns of ZnO films with five coats obtained from sols aged (a) 0, (b) 30 and (c) 60 days

crystal growth orientation, which is in a good agreement with the literature data [24, 25].

The sizes of ZnO crystallites estimated along the (101) direction (the main peak of the 60 days sample with 5 coats) by Sherrer's formula are about 8, 30 and 60 nm for the films from sols aged for 0, 30 and 60 days. The longer aging time makes the diffraction peaks (100, 002, 101) better pronounced with higher intensity and increases the size of crystallites (see Fig. 3).

Photocatalytic activity

The relationship between morphology and photocatalytic performance of synthesized ZnO films is studied as model reaction for photodegradation of pharmaceutical drugs (*Paracetamol* and *Chloramphenicol*). The photocatalytic efficiency can be influenced by two factors – one of them is aging time of the ZnO sol itself and the other factor is the influence of the PCA and CA solutions. It is

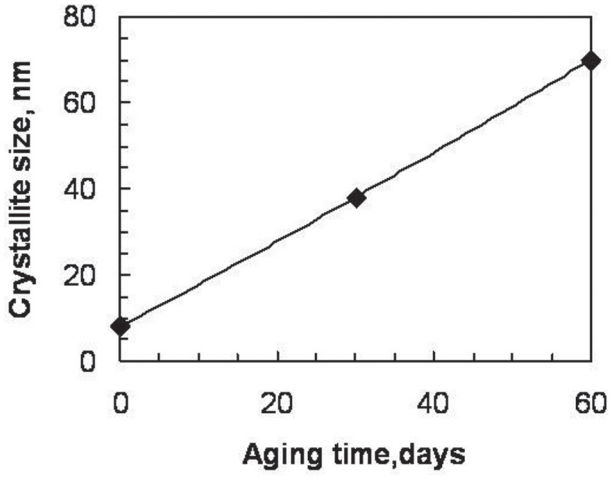

Fig. 3. Relationship between crystallite size and aging time

obvious, that these factors can not be separated completely, as the photocatalytic efficiency is measured by decomposition of the drugs.

The relationship between apparent rate constants of drugs degradation and irradiation time are presented in Fig. 4 (UV light, 4h) and Fig. 5 (visible light, 4h). The values of rate constants, k, are calculated from the corresponding $\ln(C/C_0)$ versus irradiation time:

$$\ln(C/C_0) = -kt \qquad (2)$$

where C is the initial concentration of PCA and CA at each irradiation time interval at the wavelength of 243 nm and 278 nm, C_0 is the initial concentration before the irradiation, when the adsorption – desorption equilibrium between the drug molecules and the photocatalysts nanoparticles is achieved.

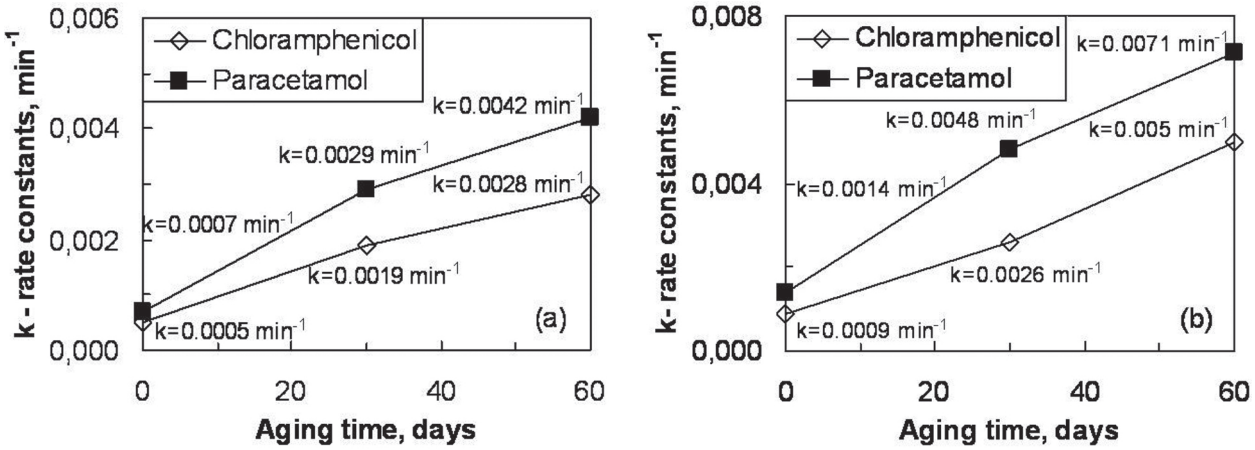

Fig. 4. Kinetic study on the photocatalytic degradation of drugs using ZnO films with 1 (a) and 5 (b) coats under UV-light illumination

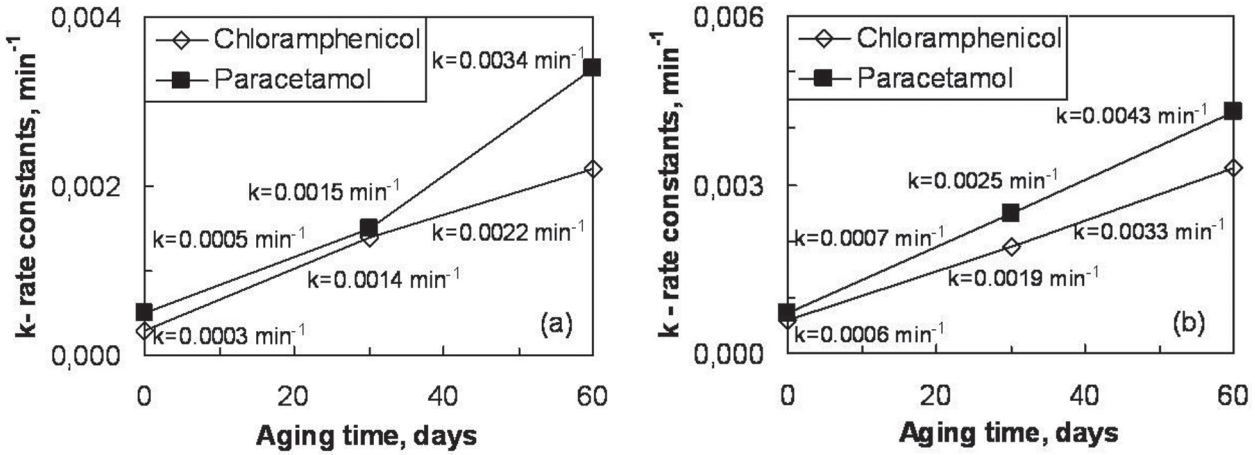

Fig. 5. Kinetic study on the photocatalytic degradation of drugs using ZnO films with 1 (a) and 5 (b) coats under visible illumination

The degradation of drugs obeys pseudo first order kinetics according to the Langmuir-Hinshelwood (L-H) model [26]. The apparent rate constant (k) is calculated by equation (2). As can be seen from Figures 4 and 5 the apparent rate constant increases with the increased aging time (in the range 0–60 days) and number of layers.

Nanostructure ZnO films deposited from 60 day aged solution have highest photocatalytic activity for degradation of the drugs under UV and visible light illumination. The samples with ZnO starting sol, aged 30 days show faster degradation of pharmaceutical products in comparison with these prepared from 0 day aged solution (Fig. 4 and 5). It is found that increasing the aging time of the starting sol increased the photocatalytic activity and the surface morphology of the samples is more developed.

The sol-gel films with five coats have higher efficiency than those prepared with one, which is probably due to the larger amount of ZnO catalyst in this case – 0.175 mg/cm^2, compared to 0.058 mg/cm^2 for the film with one coat. The largest ZnO amount is located as more developed surface of the catalysts, prepared with 5 coats. ZnO films have better photocatalytic efficiency and faster degrade PCA compared to CA. The reason for this fact is the smaller molecule of the analgesic. As confirmation of the values of rate constants is the degree of degradation of the drugs. The degradation of drugs is calculated by Eq. (1) and the results are presented in Fig. 6.

The removal (%) of PCA and CA as a function of the light exposure time for the 1 (Fig. 6 a, b) and 5 (Fig. 6 c, d) ZnO immersions, deposited from starting solutions aged at different times, namely, 0, 30, and 60 days as can be seen. From these graphs a slight degradation of drugs increasing as the number of coats increases as well can be is observed. In the case of Fig. 6c, d, corresponding to the film deposited with 5 coats from a 60-day aged solution, the most significant change occurs at PCA – under UV exposure time. A low removal of analgesic and antibiotic are reached at the not optimized conditions (0 day).

When more aged solution is used, the films present a higher photocatalytic activity, as can be observed in Figures 4–6. According to our results, the ZnO films with a very rough surface present a better degradation of drugs than those with a smoother surface. The more developed surface increases the total illuminated surface area, thus increasing the number of active surface sites and enhancing the catalytic activity of the films, as has been also established by Aprile et al. [27]. Taking this into account, we

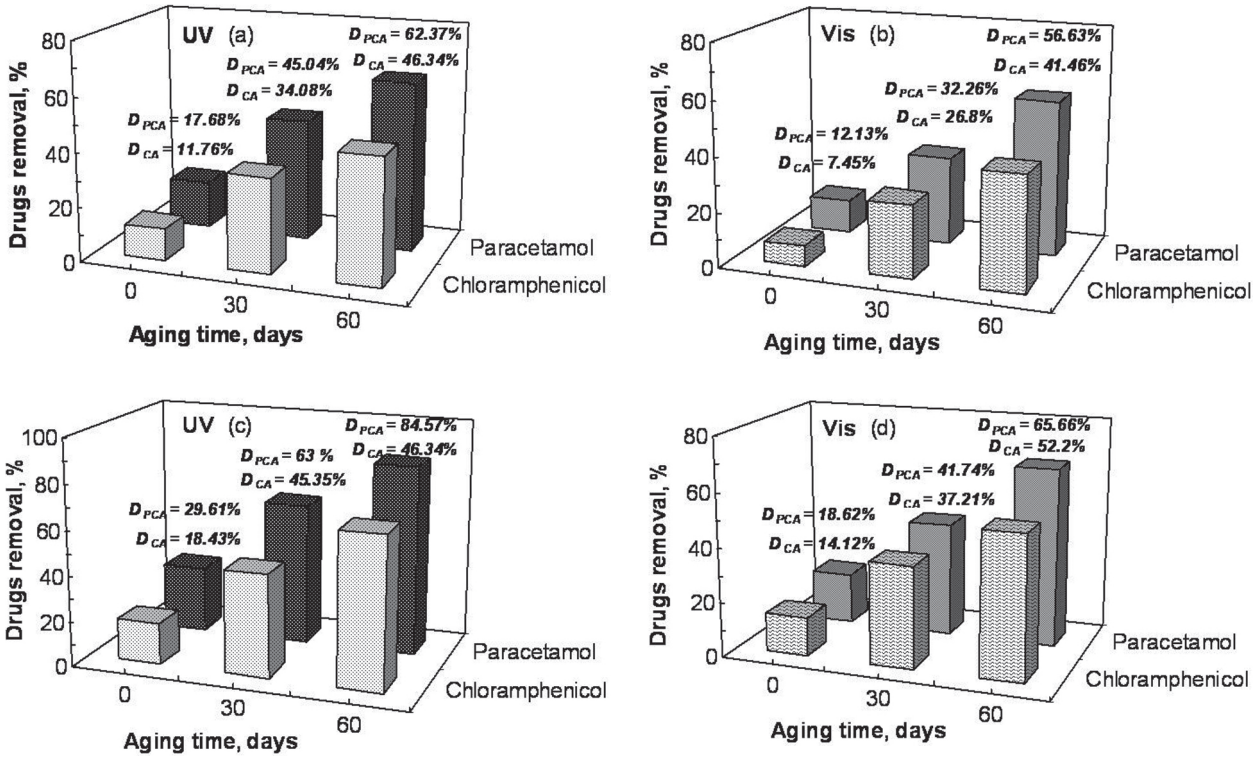

Fig. 6. Photocatalytic mineralization of Paracetamol and Chloramphenicol under UV and visible illumination using ZnO films with 1 (a, b) and 5 (c, d) coats

can consider that the formation of spatial structures promote the photocatalytic activity by increasing the exposed area and enhancing the mean life of the photo-generated holes

CONCLUSIONS

ZnO thin films on glass substrates are deposited by sol–gel technique starting from zinc acetate dehydrate dissolved in 2-methoxyethanol and monoethanoamine. The samples with different aging time (ZnO sol, stored 0, 30 and 60 days) have a ganglia-like surface, which are obtained by this simple and economical method. The film thickness and the aging time of the starting solution play an important role in the degradation performance of *Paracetamol* and *Chloramphenicol*. A 85% of analgesic and 67% of antibiotic degradation is reached using ZnO thin films with five coats, starting sol stayed 60 day, under UV-irradiation. Our investigation shows that aging time and thickness of ZnO thin films play significant role in the photocatalytic process.

Acknowledgements: *This research is financially supported by project DFNIT0216, FP7 project Beyond Everest and Russian Presidential Program of engineer advanced training.*

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ЕФЕКТ НА СТАРЕЕНЕ НА ЗОЛ ВЪРХУ СТРУКТУРАТА И ФОТОКАТАЛИТИЧНАТА АКТИВНОСТ НА ZnO ФИЛМИ ЗА РАЗГРАЖДАНЕ НА ФАРМАЦЕВТИЧНИ ЛЕКАРСТВА

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

Лаборатория по Наука и Технология на Наночастиците, Катедра по Обща и неорганична химия, Факултет по Химия и Фармация, Софийски университет, бул. "Джеймс Баучер" 1, 1164, София, България

Постъпила декември, 2014 г.; приета януари, 2015 г.

(Резюме)

В тази работа, ZnO тънки филми са получени чрез зол-гел метод и ефекта на стареене на ZnO зол е изследван върху структурата и фотокаталитичните свойства на филмите. ZnO зол е престоял различно време (0, 30 и 60 дни). Нанокристалните тънки филми с различна дебелина (едно и пет покрития) са отложени върху стъклени подложки чрез метода на потапящата подложка. Структурните свойства на пробите са анализирани чрез Сканиращ Електронен Микроскоп и Рентгенова дифракция. Ефектът на стареене на изходния зол е изследван за фотокаталитичното разграждане на фармацевтични лекарства (*Парацетамол (ПЦА)* и *Хлорамфеникол (ХА)*) посредством УВ-вис спектроскопия. Експериментите са проведени под действието на ултравиолетова и видима светлина. Резултатите показват, че с повишаване времето на стареене на изходния ZnO разтвор обикновено се увеличава фотокаталитичната активност. Филмите с едно покритие имат по-ниски скоростни константи при разграждането в сравнение с останалите проби. Тънките филми с пет слоя получени от ZnO зол, престоял 60 дни показват най-високо фотокаталитично разграждане на лекарствата (*ПЦА*: УВ – 84.57% и Видима – 65.66 %; *ХА:* УВ – 67.2% и Видима – 52.2%) в сравнение с тези получени с едно (*ПЦА*: УВ – 29.60% и Видима – 18.62%; *ХА*: УВ – 18.43% и Видима – 14.12%).