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Effect of thickness on the photocatalytic properties of ZnO thin films

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Nanostructured zinc oxide films are prepared by sol-gel method using dip-coating technique. The thin films are deposited on glass substrates with different thickness (1, 3, 5 and 7 coats). The samples are characterized by means of XRD, SEM and UV-visible analyses. The aim of our investigations is photocatalytic degradation of the organic dyes – *Malachite Green* (MG, triarylmethane azo dye) and *Methylene Blue* (MB, heterocyclic aromatic dye) under UV-light illumination.

The photocatalytic results show that the thickest films on glass exhibit the highest efficiency under UV-light. The thin films with one coating have lowest rate constants in comparison with the other samples. The ZnO films with 7 coats have better photocatalytic efficiency and faster degradation of MG compared to MB, reasoned by the formation of stable intermediates in the reaction of OH radicals with triarylmethane dye (C=C bond) during the photocatalysis.

Key words: ZnO, thin films, thickness, photocatalysis, sol-gel, organic dyes.

INTRODUCTION

In the past decades, environmental problems have been increasingly serious with the development of the industry of human society. Eradication of toxic compounds from water and wastewater has become the focus of research recently.

Textile dyes are of environmental interest because of their widespread use and their potential for forming toxic aromatic amines. Among the synthetic dyes, which are widely used for textile dyeing and other industrial applications, those containing an azo chromophore constitute the largest class [1]. Azo dyes are a class of dyes, which are widely used in a variety of products, such as textiles, paper, foodstuffs or leather. However, these compounds and degradation products can be hazardous because their toxicity and carcinogenicity. Excess use of various dyes in the textile industry has led to the severe surface water and groundwater contamination by releasing the toxic and colored effluents [2]. It is important for the sake of increasing amount, its variety and resistance to biological destruction [3].

Many dye pollutants can be degraded effectively and ultimately mineralized using Advanced Oxidation Processes" (AOP). Heterogeneous photocatalysis as an advanced oxidation process [4] for wastewater treatment involves degradation of organic pollutants form wastewater using semiconductor oxides powders or suspensions. The catalytic materials applied in such studies have drawbacks like catalyst agglomeration, difficulty in post operation recovery and reuse as well as environmentally safe disposal. To circumvent these limitations, immobilizing the photocatalyst as thin films over large transparent supports is a viable option. ZnO thin films can be prepared by a number of methods including chemical vapor deposition (CVD) [5, 6], spin coating [7, 8], magnetron sputtering [9, 10], sol-gel method [11–13], pulsed laser deposition (PLD) [14, 15] and plasma-assisted molecular beam epitaxy (P-MBE) [16]. The sol-gel process is very attractive low-cost and versatile method for deposition of homogeneous thin films with desired thickness and nanostructure.

ZnO has a competitive photocatalytic activity greater in some cases than TiO_2; for example,

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on the discoloration of Reactive Blue 19, a textile anthraquinone dye, in aqueous suspension [17]. Furthermore, ZnO thin films have been found to decompose aqueous solutions of azo [18] and textile dyes [19], as well as phenol [20] and pharmaceutical drugs [21, 22]. Despite the importance of ZnO in the photocatalytic processes, little work has been done on ZnO thin films and their photocatalytic properties.

In this study, low cost sol-gel method is used to synthesize ZnO films over glass substrate via dip-coating technique. The thin films are obtained with different thickness and used as catalysts for photodegradation of *Malachite Green* and *Methylene Blue*.

MATERIALS AND METHODS

Materials

All reagents were used as received and purchased from Fluka. Zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$, ≥99.5% purity) was used as a zinc source. As a dispersing medium, 2-methoxyethanol ($C_3H_8O_2$, ≥99.5% purity) has an important role as the solvent and monoethanolamine (MEA, $HOCH_2C_2NH_2$, ≥99.0% purity) as stabilizer. The glass slides (ca. 76×26 mm) for substrates of ZnO films were from ISO-LAB (Germany). *Malachite Green* ($C_{52}H_{54}N_4O_{12}$, λ_{max} = 615 nm, Chroma-Gesellschaft mbH&Co) and *Methylene Blue* ($C_{16}H_{18}ClN_3S$, λ_{max} = 660 nm, Fluka) were model pollutants and representatives of the most important impurities in the textile industry wastewater. Distilled water was used in the preparation of dye solutions.

Methods

Synthesis and characterization of ZnO films

The method of preparing sols and thin films was the same as procedure, carried out in previous works and was described briefly as following [18, 23]: In order to prepare the samples, zinc acetate dehydrate was dissolved in 2-methoxyethanol under vigorous magnetic stirring for a few minutes at room temperature to obtain a homogeneous medium. The equimolar quantity mole of monoethanolamine was added to the solution (molar ratio of zinc acetate to MEA was 1:1). The reaction mixture solution was stirred by a magnetic stirrer at 500 rpm to yield homogeneous solution and heated at 60 °C for 1 h. Afterwards the solution was kept in a covered for 24 h at room temperature. No visible changes were observed in the sol upon storing of the precursor for at least 2 months. The glass substrates were rinsed in distilled water. The thin films were prepared by dip-coating technique with withdrawal speeds of 0.9 cm/min at room temperature. After dip-coating process, the samples were dried at 80 °C for 15 min. This coating procedure was repeated 1, 3, 5 and 7 times. Finally, the films were annealed at 500 °C for 1 hour in order to obtain the ZnO films for photocatalytic experiments. The mass of ZnO deposited on films prepared with a single and seven coatings was 2.06 mg (± 8 %) and 7.88 mg (± 6%), respectively. The film area was about 14.5 cm^2 on each side of the glass plate.

The obtained ZnO thin films were characterized by powder X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM). The XRD spectra were recorded 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). The average size of crystallites is calculated by the Scherer's equation:

$$d_{hkl} = k\lambda/\beta \cos(2\theta) \quad (1)$$

where d_{hkl} is the average crystallite size (nm), λ is the wavelength of CuKα radiation applied (λ = 0.154056 nm), θ is the Bragg's angle of diffraction, β is the full-width at half maximum intensity of the most intensive 101 peak observed at 2θ = 36.2° (converted to radians) and k is a constant usually chosen ~0.9.

The SEM images were obtained by scanning electron microscope JSM-5510 (JEOL) operated at 10 kV of acceleration voltage. The investigated samples were coated with a thin film of gold by fine coater JFC-1200 (JEOL) before observation.

Photocatalytic experiment

The photocatalytic activity of the sol-gel films with different thickness were evaluated by the photocatalytic purification of model pollutants: *Malachite Green* (MG) and *Methylene Blue* (MB) were used as organic materials to be mineralized under UV-light illumination. The light power density at the sample position was 0.66 mW/cm^2 measured with research radiometer (Ealing Electro-optics, Inc.). The lamp was fixed at 15 cm above the treated solution. The initial concentration of MG and MB were 10 ppm. All photocatalytic experiments were performed at ambient temperature (23 ± 2 °C).

The ZnO films were placed in glass reactor containing 150 mL 10 ppm dyes solution and were then irradiated with light source (Sylvania 18 W BLB T8). The films were placed at 0.5 cm below the surface of the investigated solution. This tube emits UVA in the range of 315–400 nm. After irradiating for 4 h, the concentration of the residual MG and

MB were determined by a UV–Vis spectrophotometer (Evolution 300 Thermo Scientific) at λ_{max} = 615 nm and λ_{max} = 660 nm. The rate of decolorization was observed in terms of change in intensity at λ_{max} of the dyes. The decolorization efficiency (D %) was calculated using the equation:

$$D\% = \frac{C_0 - C_t}{C_t} x100 \qquad (2)$$

where C_0 and C_t were initial and instantaneous concentrations of MG and MB.

RESULTS AND DISCUSSION

Structure and morphology of ZnO films

The phase structure and orientation of the ZnO films with 1 and 7 coats on glass substrate are determined by X-ray diffraction (XRD) and the diffractogram is presented in Fig. 1. The films produced are polycrystalline, showing the wurtzite ZnO hexagonal structure, while there is no evidence for the presence of other phases. All the diffraction peaks of the ZnO thin films can be indexed to (100), (002), (101), (102), (110), (103), (200), (112) and (201) diffraction planes at 2θ = 31.77°, 34.42°, 36.25°, 47.54°, 56.60°, 62.86°, 66.37°, 67.96° and 69.09°, respectively. The most intensive (101) peak is observed at $2\theta = 36.2^{o}$. The size of crystallites of the all thin films, calculated by Scherer (Eq. 1) from the (101) peak is ~30 nm.

SEM image of the surface of the samples with one and seven coatings synthesized via sol-gel method is presented in Fig. 2. As seen in the figure, the investigated films has homogeneous surface with different ganglia-like hills. The morphology is

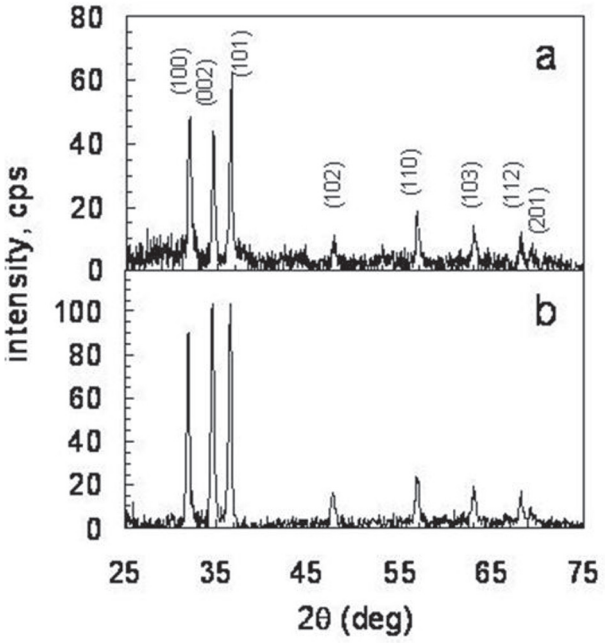

Fig. 1. XRD pattern of sol-gel film with one (a) and seven (b) coats

homogenous with the wrinkles, which are located on the films surface. Their shape, size and thickness are changed, depending of number of coats (Fig. 2a). The surface of films with seven coats is much more developed (Fig. 2b). The wrinkles are bigger (typical height about 2.5–3μm, width 1μm and length from 5 to 15 μm) and the morphology is homogenous. The thin films show much better adhesion of the layers and higher density, compared to films with one coat. They are reproducible irrespective on the conditions of film deposition (with

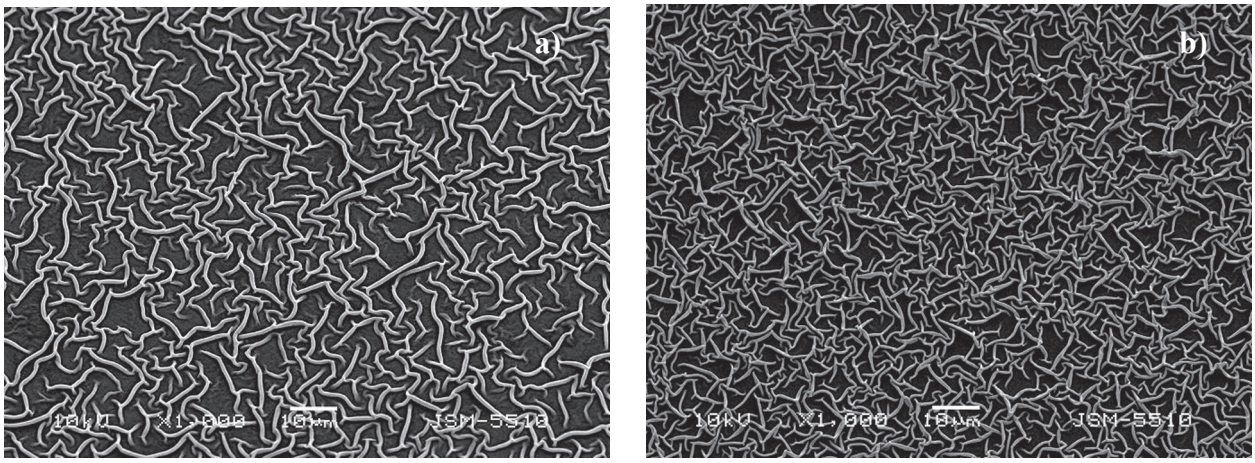

Fig. 2. SEM image of ZnO film with one (a) and seven (b) coats

different thickness) and we can see them in always different films [18, 23].

Photocatalytic properties

The photocatalytic efficiency depends on many parameters such as the distance between light source and organic compound, light intensity, initial concentration of dyes, doped and pure photocatalysts, different thickness of materials, pH and so on. In this work, the effect of thickness on the photocatalytic activity of ZnO films is studied for degradation of Malachite Green and Methylene Blue. The photocatalytic activity of the ZnO sol-gel films with different thickness are evaluated by the photocatalytic degradation of MG and MB as representative dye pollutants. The photocatalytic decolorization of dyes is believed to take place according to the following mechanism [24]:

$$ZnO \rightarrow e^{-}_{CB} + h^{+}_{VB} \quad (3)$$

$$e^{-}_{CB} + O_2 \rightarrow O_2^{\bullet -} \quad (4)$$

$$h^{+}_{VB} + OH^{-} \rightarrow OH^{\bullet} \quad (5)$$

$$O_2^{\bullet -} + H_2O \rightarrow HO_2^{\bullet} + OH^{-} \quad (6)$$

$$HO_2^{\bullet} + H_2O \rightarrow H_2O_2 + OH^{\bullet} \quad (7)$$

$$H_2O_2 \rightarrow 2OH^{\bullet} \quad (8)$$

$$OH^{\bullet} + dye \rightarrow CO_2 + H_2O \quad (9)$$

where h^{+}_{vb} and e^{-}_{cb} are the electron vacancies in the valence band and the electron in the conduction band, respectively.

Several reports claim that the rate of photocatalytic degradation of various dyes fitted a pseudo first order kinetic model [25, 26]:

$$r = -\frac{dC}{dt} = k \quad (10)$$

Integrates Eq. (10), giving

$$-Ln\frac{Ct}{C_0} = k \quad (11)$$

where C_0 is the initial concentration of MG and MB, C_t is the concentration of dyes at irradiation time t, t is the irradiation time and k is the apparent pseudo first order rate constant. The photocatalytic degradation of the dye solutions over all illuminated ZnO thin films with different thickness obeyed pseudo first order kinetics. Figure 3 shows the pseudo first order reaction with respect to the change of dyes concentration under UV-light illumination. The relationship between thickness and photocatalytic properties of ZnO films is summarized and compared for the both dyes in Fig. 4. As seen from figure, the thickest films have the highest rate constants and photocatalytic properties. This dependence is observed in the mineralization of the two dyes. The photocatalytic degradation is highest for the films obtained by seven coatings, which is probably due to the largest amount of ZnO catalyst. The films with three layers have higher efficiency than those, prepared with one. The rate constants

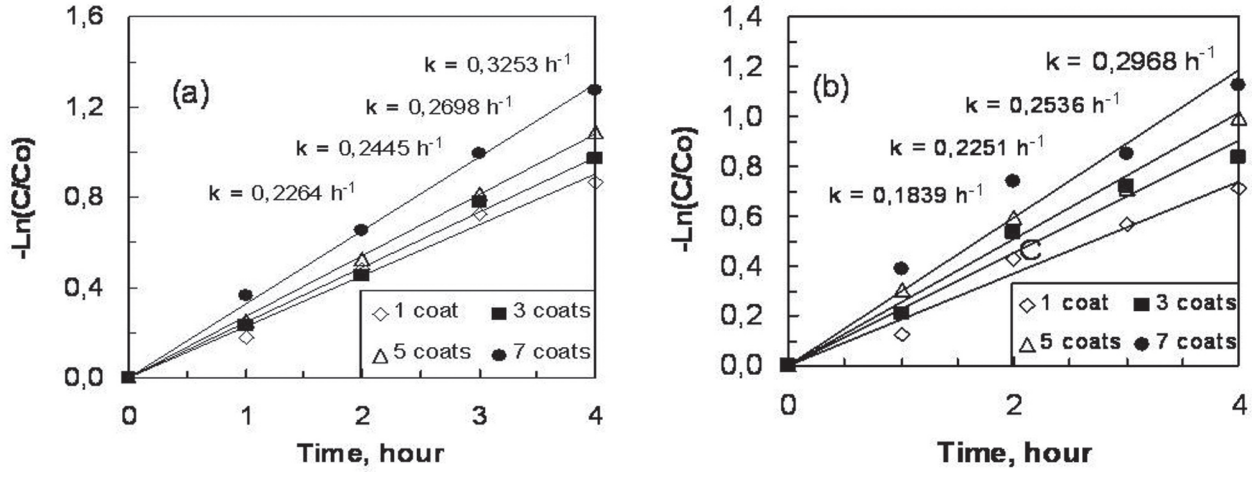

Fig. 3. Kinetic study on the photocatalytic degradation Malachite Green (a) and Methylene Blue (b) using ZnO thin films with different thickness (1, 3, 5 and 7 coats)

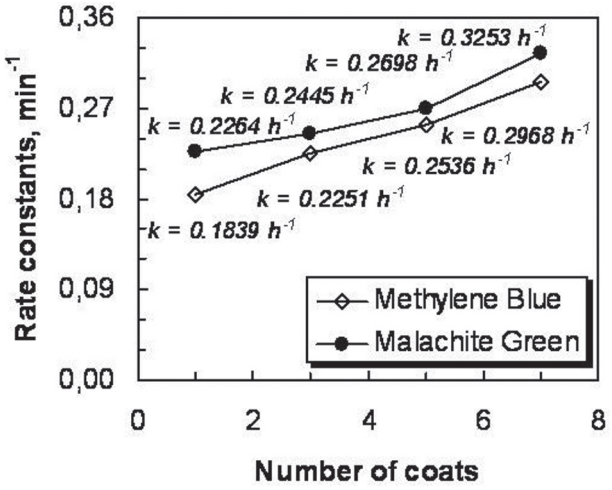

Fig. 4. Relation between rate constants and different thickness of ZnO films for the degradation of dyes under UV-light illumination

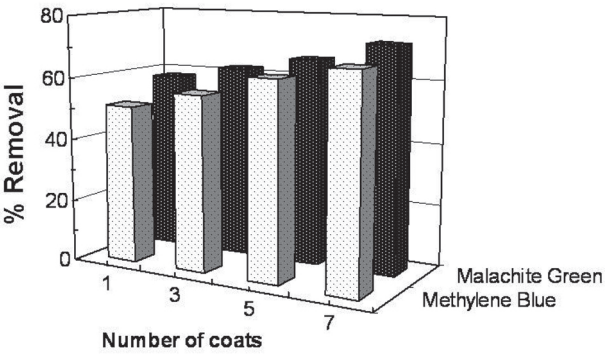

Fig. 5. Effect of the thin films with different thickness on photocatalytic mineralization of Malachite Green and Methylene Blue

are increased in the intermediate thickness – 3 and 5 coats. These results confirm that the rise in thickness of ZnO films leads to increases of the activity. The observed faster degradation of MG compared to MB most probably is due to the formation of a stable intermediates in the reaction of OH radicals with triarylmethane dye (C=C bond) during the photocatalysis [26, 27]. The values *k* of the rate constants are confirmed by rate of degradation of the organic dyes. The degradation is calculated using Eq. 2.

Nanostructured films with 7 layers have a better photocatalytic activity and faster degradation MG (*D%* = 72.11% for four hours) in comparison with MB (*D%* = 67.43% for four hours) (Fig. 5). The photocatalytic activity is highest for the films obtained by seven coats, while samples obtained with one layer have a lowest activity ($D\%_{MG}$ = 58.04% and $D\%_{MB}$ = 50.84%, Fig. 5). The reason is probably due to the larger amount of ZnO catalyst – 0.230 mg/cm^2 compared to 0.175 mg/cm^2 (film with 5 coats), 0.126 mg/cm^2 (film with 3 coats) and 0.058 mg/cm^2 (film with 1 coat).

Probable mechanisms of degradation of MB and MG, induced by a reaction with hydroxyl radicals, have been reported in the literature [27, 28]. Regarding MB, Houas et al. [26] suggested that in the initial step HO• radical cleavages S+=C double bond, which in turn induces ring-opening reaction of the central heterocyclic moiety, thereby leading to decolourization of the solution (Fig. 6a). In an-

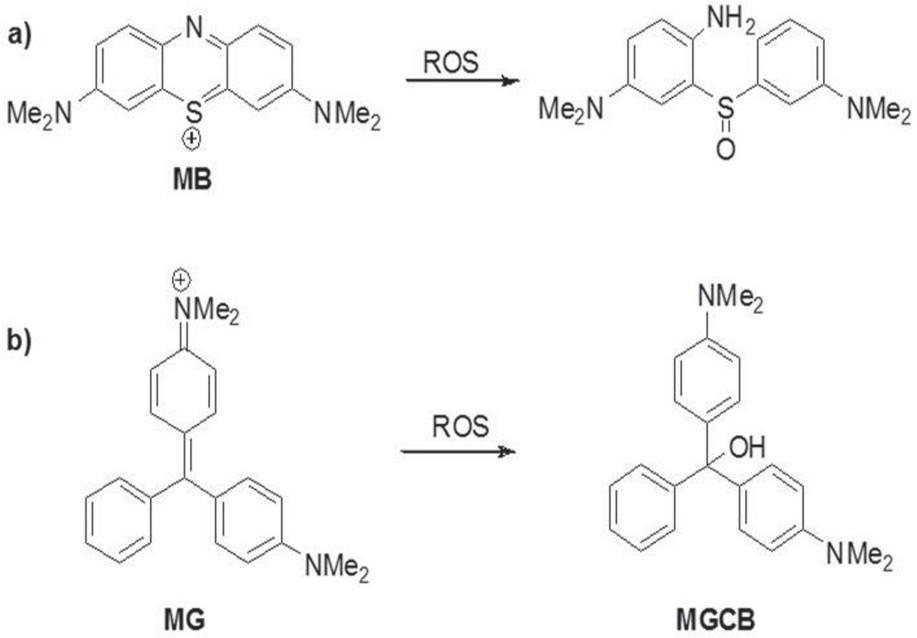

Fig. 6. First step of decomposition of: a) Methylene Blue (MB) and b) Malachite Green (MG)

other study, Ju et al. [28] showed that the initial step of MG degradation includes radical attack on the central carbon of MG, which transforms it into malachite green carbinol base (MGCB) and again leads to decolourization of the solution (Fig. 6b). Taking into account the above reasoning, it can be concluded that the faster degradation of MG, observed in the present study, can be attributed to the facilitated attack of HO• radical toward the sulfur atom, the latter being due to its enhanced electron density.

CONCLUSION

Nanostructure ZnO films are obtained by sol-gel method from zinc acetate dehydrate dissolved in 2-methoxyethanol and monoethanolamine. The samples onto glass substrates are deposited with different thickness (1, 3, 5 and 7 coats) via dip-coating technique. The film thickness plays an important role in the degradation performance of *Malachite Green* and *Methylene Blue*. The photocatalytic results show that the films with seven coats show better efficiency and faster degradation MG compared to MB under UV-light. The thin films with one layer have lowest photocatalytic behavior for mineralization of dyes in comparison with the other samples. The optimal thickness of films is experimentally established. A 72% of MG and 67% of MB decolorization is reached with the thickest ZnO photocatalysts under UV-light irradiation. The photocatalytic processes show that ZnO films with different thickness are attractive for application in wastewaters.

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ЕФЕКТ НА ДЕБЕЛИНАТА ВЪРХУ ФОТОКАТАЛИТИЧНИТЕ СВОЙСТВА НА ZnO ТЪНКИ ФИЛМИ

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(Резюме)

Наноструктурираните цинк оксидни филми са получени чрез зол-гел метод използвайки метода на потапящата подложка. Тънките филми са отложени върху стъклени подложки с различна дебелина (1, 3, 5 и 7 покрития). Пробите са характеризирани основно чрез XRD, SEM и UV-visible анализи. Целта на нашите изследвания са фотокаталитично разграждане на органични багрила– *Малахитово Зелено* (МЗ, триарилметаново азо багрило) и *Метиленово Синъо* (МС, хетероциклено ароматно багрило) под действието на ултравиолетова светлина.

Фотокаталитичните резултати показват, че най-дебелите филми върху стъкло притежават най-висока ефективност под ултравиолетова светлина. Тънките филми с едно покритие имат най-ниска скоростна константа в сравнение с останалите проби. ZnO филми със седем слоя има по-висока фотокаталитична ефективност и по-бързо разграждат МЗ в сравнение с МС, доказано чрез образуването на стабилни междинни продукти в реакцията на ОН радикали с триарилметановото багрило (C=C връзка) по време на фотокатализата.