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Effect of Precursors Aging Time on the Photocatalytic Activity of ZnO Thin Films

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***Abstract*—**Thin ZnO films are deposited on glass substrates via sol–gel method and dip-coating. The films are prepared from zinc acetate dehydrate as a starting reagent. After that the as-prepared ZnO sol is aged for different periods (0, 1, 3, 5, 10, 15 and 30 days).

Nanocrystalline thin films are deposited from various sols. The effect ZnO sols aging time on the structural and photocatalytic properties of the films is studied. The films surface is studied by Scanning Electron Microscopy. The effect of the aging time of the starting solution is studied in the photocatalytic degradation of Reactive Black 5 (RB5) by UV-vis spectroscopy. The experiments are conducted upon UV-light illumination and in complete darkness. The variation of the absorption spectra shows the degradation of RB5 dissolved in water, as a result of the reaction, occurring on the surface of the films and promoted by UV irradiation. The initial concentrations of dye (5, 10 and 20 ppm) and the effect of the aging time are varied during the experiments. The results show, that the increasing aging time of starting solution with respect to ZnO generally promotes photocatalytic activity. The thin films obtained from ZnO sol, which is aged 30 days have best photocatalytic degradation of the dye (97,22%) in comparison with the freshly prepared ones (65,92%). The samples and photocatalytic experimental results are reproducible. Nevertheless, all films exhibit a substantial activity in both UV light and darkness, which is promising for the development of new ZnO photocatalysts by sol-gel method.

***Keywords*—**ZnO thin films, sol-gel, photocatalysis, aging time.

I. Introduction

TEXTILE industry wastewater is heavily charged with unconsumed dyes, surfactants and sometimes traces of metals. These effluents cause a lot of damage to the environment. In most countries researchers are looking for appropriate treatments in order to remove pollutants, impurities and to obtain the decolorization of dye house effluents [1]–[3]. Usually, the conventional biological treatment processes do not readily remove dyes from textile wastewater, because of their resistance to biological degradation [4], [5]. Various chemical, physical and biological processes are currently used such as flocculation, ultrafiltration, adsorption, ozonation and chlorination [6].

These processes are not efficient because they appear in solid wastes, thus creating other environmental problems requiring further treatment. Therefore, it is necessary to find an effective method of wastewater treatment in order to remove hazardous dyes and organics from industry effluents [4]. One of the effective methods of wastewater treatment containing dyes is their photocatalytic degradation in solutions illuminated with UV irradiation, which contains a suitable photocatalyst, such as zinc oxide (ZnO) [7], indium oxide (In_2O_3) [8], tin oxide (SnO_2) [9] and titanium oxide (TiO_2) [10] has notably increased. These materials in thin film form present transport and optical properties that make them good candidates in modern applications. From these oxides, ZnO is a well-known chemically stable material commonly used as coating material in optical thin films. ZnO has also received extensive attention due to its excellent photocatalytic properties.

Photocatalytic processes in polluted air and water through the use of UV-irradiated inorganic oxides degrade the concentration of contaminants. ZnO has a competitive photocatalytic activity greater in some cases than TiO_2; for example, on the discoloration of Reactive Black 5, textile anthraquinone dye, in aqueous suspension [11] and in the oxidation of protocatechuic acid [12]. Furthermore, ZnO thin films have been found to decompose aqueous solutions of reactive dyes [13], [14], as well as phenol and chlorophenol [15] and other environmental pollutants [16]. Despite the importance of ZnO in the photocatalytic processes, little work has been done on ZnO thin films and their photocatalytic properties. To our knowledge, we have found some reports on photocatalysis using ZnO thin films, in which the films are prepared by different techniques such as metal organic chemical vapor deposition [17], sol–gel [18], [19], thermal evaporation, oxidation and anodizing [20]–[22]. Many results about effects of ZnO sol concentration and annealing treatment on ZnO thin films have been reported, but the effect of ZnO sol aging time on the quality of ZnO thin films for photocatalytic applications is seldom studied. In the process of aging, some properties of the sol will be change. Therefore, to study the effect of sol aging time on the quality of ZnO thin films is important. The sol–gel process is one of the most appropriate methods to prepare thin oxide coatings due to its several advantages, such depositions with good homogenate, low processing temperature, low equipment cost and good optical properties. The preparation conditions of ZnO thin films with the sol– gel method can influence the physical and photocatalytic properties of the film.

In this work, ZnO thin film are prepared by sol-gel method and the effect of aging time of ZnO starting sol (0, 1, 3, 5, 10, 15 and 30 days) on the structure and photocatalytic properties of the films is studied. The deposited ZnO thin films are used

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for the degradation of Reactive Black 5, which is one of the textile dye. Photocatalytic tests are conducted under UV-light illumination and in complete darkness. Our previous studies have shown that the sol is stable and no precipitation for up to one month. The photocatalytic experiments are repeated three times, using in each cycle new dye solution with the same initial concentration. All the tests are reproducible.

II. Experimental

A. Materials and Reagents

The materials used to manufacture the ZnO thin films were described as follows: Zinc acetate dihydrate (≥99.5%), 2methoxyethanol (≥99.5%) and monoethanolamine (≥99.0%). Reactive Black 5 ($C_{26}H_{21}N_5Na_4O_{19}S_6$, λ_{max}=595 nm, dye content ca. 55%) was from Sigma-Aldrich. Glass slides (ca. 76x26 mm) used for substrates of ZnO films were from ISOLAB (Germany). Distilled water was used in the preparation of dye solutions.

B. Preparation of Thin Films

Zinc oxide thin films were prepared on glass substrate by sol gel method. The sol was prepared using zinc acetate dihydrate, 2-methoxyethanol and monoethanolamine [23]. Zinc acetate ($Zn(CH_3COO)_2.2H_2O$) were dissolved in 2-methoxyethanol, and then monoethanolamine (MEA) was added to the solution as a stabilizer. The substances were mixed together in a round-bottomed flask and stirred at room temperature for 15 min. The obtained clear solution was heated up at 60°C upon magnetic stirring for 1 hour and let overnight. The resultant solution was clear and homogenous, and served as the coating substance for the film preparation. No visible changes were observed upon standing of the precursor at room temperature for at least 2 months.

The ZnO sol was aged for 0, 1, 3, 5, 10, 15 and 30 days, respectively. Then ZnO thin films were prepared via dip coating technique on glass substrates which had been cleaned thoroughly and dried. Dipping glass substrate in the precursor solution and withdrawing it at rates of 0.9 cm/min at room temperature prepared the gel films. It was experimentally found that higher withdrawal rates resulted in films of lower quality. This method of deposition is simple and inexpensive, but requires soluble reagents. Films were deposited with 5 coatings at the different aged time. The films were dried at 80°C for 30 min after each successive coating. The final gel films were annealed at 500°C for 1 hour in order to obtain the ZnO films for photocatalytic tests.

C. Characterization of ZnO Films

The surface morphology of ZnO thin films at different aging time were characterized by Scanning Electron Microscope (SEM, JEOL JSM-5510), operated at 10 kV of acceleration voltage. The investigated samples were coated with gold by JFC-1200 fine coater before observation.

The X-Ray diffraction (XRD) spectra were recorded at room temperature on a 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 was estimated according to Scherrer's equation [24]:

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

where d_{hkl} is the average crystallite size (nm), λ the wavelength of the CuKα radiation applied (λ = 0.154056 nm), θ the Bragg's angle of diffraction, β the full-width at half maximum intensity of the peak observed at 2θ = 25.20 (converted to radian) and k is a constant usually applied as ~0.9.

Dye concentration in the aqueous solution after irradiation and the optical absorbance spectra were measured by spectrophotometer Jenway 6400 in the wavelength range from 400 to 800 nm.

D. Photocatalytic Degradation of Reactive Black 5

Reactive Black 5 (RB5) is common chemical that is used extensively in variety of industrial applications. Therefore, it is chosen to be as a model pollutant to test the photocatalytic activity.

The photocatalytic performance of the films was determined by the degradation of RB5 dye solution. The photocatalytic reaction was conducted in glass reactor (250 ml), equipped with a 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/cm2 as measured with Research Radiometer of Ealing Electro-optics, Inc.). The decay of RB5 concentration during the bleaching process was monitored by UV-vis absorbance spectroscopy after aliquot sampling at regular time intervals. Control experiments in darkness were also performed. The photodegradation efficiency has been calculated as:

$$\%D = \frac{C_0 - C}{C} x100 \quad (2)$$

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

Experiments were carried out with seven series: nanostructured ZnO films obtained at different aging time of the starting solution (0, 1, 3, 5, 10, 15 and 30 day), prepared with 5 coatings. The effect of initial concentration of RB5 (5, 10 and 20 ppm) was also evaluated. All photocatalytic tests were performed at constant stirring rate (500 rpm) at room temperature (23±2°C).

III. Results

A. The Microstructure of the Prepared ZnO Thin Films

The morphology of seven type ZnO thin films are characterized by SEM (Fig. 1). These micrographs clearly show that there are changes in the surface of the films. Fig. 1 (a) shows the surface morphology of ZnO thin film, where a very smooth surface, covered by round grains. The formation of very smooth surfaces is a key factor in some applications, but not for the photocatalysis. Therefore, the films have the lowest activity. Fig. 1 (b) shows the morphology surface of other zinc oxide film, which is not smooth. The scanning

electron microscopy of the ZnO films (ZnO sol stayed 1 day) reveals ganglia-like structure. The morphology is homogenous with the wrinkles. Their shape, size and thickness are changed, depending of the aging time of the starting solution. The increase of stayed time of ZnO sol increases the volume and size of ganglia-like hills (Figs. 1 (b)-(g)), which are looking more distorted and branched at their ends. The wrinkles are bigger and the morphology is homogenous. The ganglia-like structure seems reproducible irrespective on the conditions of film deposition and annealing.

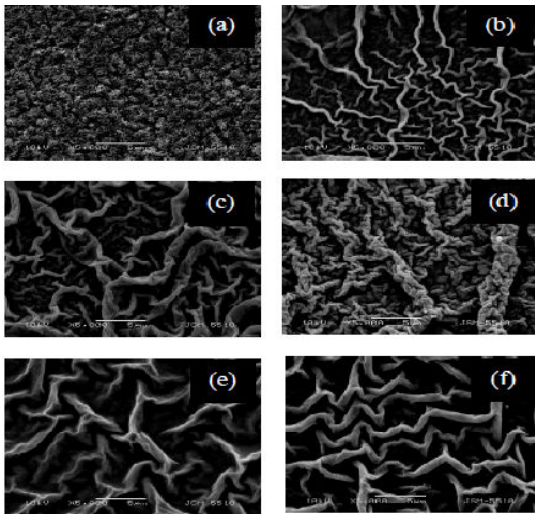

Fig. 1 SEM images of ZnO thin films obtained from sols, which were aged for: (a) 0 day, (b) 1 day, (c) 5 days, (d) 10 days, (e) 15 days and (f) 30 days, respectively

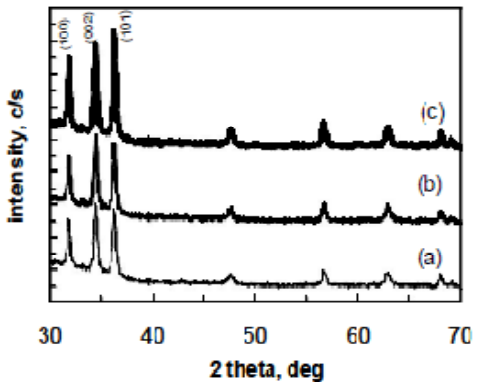

Fig. 2 XRD pattern of the prepared ZnO thin films, which were aged for (a) 0 day, (b) 10 day and (c) 30 day

Figs. 2 (a), (b) show the XRD data of ZnO films at 0 and 10 day aged solution. The films show a diffraction peak at 34.4° or so, which corresponds to the reflection of the (002) plane of wurtzite-structured ZnO. This suggests that all the samples have a wurtzite structure and are preferentially oriented along the c-axis which is perpendicular to the substrate surface. This result is confirmed [25]. Fathollahi and Amini think that the sol aging can cause further condensation of the active groups and aggregation of zinc species in the solution and consequently may lead to the significant growth of the zinc oxide (002) reflection [25]. Both we and Fathollahi and Amini found that the sol aging can improve the degree of preferred crystal orientation along the c-axis, and it did not change the crystal growth orientation.

Nanostructured ZnO thin films obtained at 500°C by 10-day aged solution is preferentially oriented along the (002) direction, but the ZnO thin films deposited by the starting solution with aging time more than 1 day were preferentially oriented along the (101) direction in turn. The results are similar to reported by [26] and [27] prepared ZnO thin films by spray pyrolysis, they found the aging time of the starting solution had a great effect on the crystal growth orientation. The average sizes of crystallites are 8, 30 and 60 nm (for the films at 0, 10 and 30 days aged solution). The rise aging time makes the diffraction peaks better pronounced and increases the size of crystallites. The relationship between aged time and corresponding ZnO crystallite sizes are summarized and illustrated in Fig. 3. As seen from the figure, the average sizes of the crystallites are increased in the intermediate aged time – 3 and 15 day (from 15 nm to 40 nm). These results further confirm that an increase in aged time increases the size of crystallites.

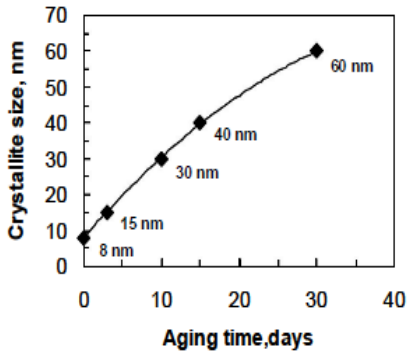

Fig. 3 Relationship between the crystallite size of ZnO and the agint time for the thin films on glass substrates

In spite of the deposition technique difference, all the above mentioned results show that the aging time of the starting solution have influence on the structures and photocatalytic activity of ZnO thin films. As for the sol–gel method, our results suggest 30days aged ZnO sol is ideal for fabrication of high-quality ZnO thin films.

B. The Aging Effect of Photocatalytic Activity of ZnO film

Photocatalytic decomposition of Reactive Black 5 is used to evaluate the photocatalytic activity of the synthesized ZnO structures. It is well known that the photocatalytic decomposition of organic pollutants accords with a pseudo first-order kinetic under UV-light illumination (Figs. 4 (a) and 5 (a)). In tests conducted in the dark is observed first order kinetics (Figs. 4 (b) and 5 (b)).

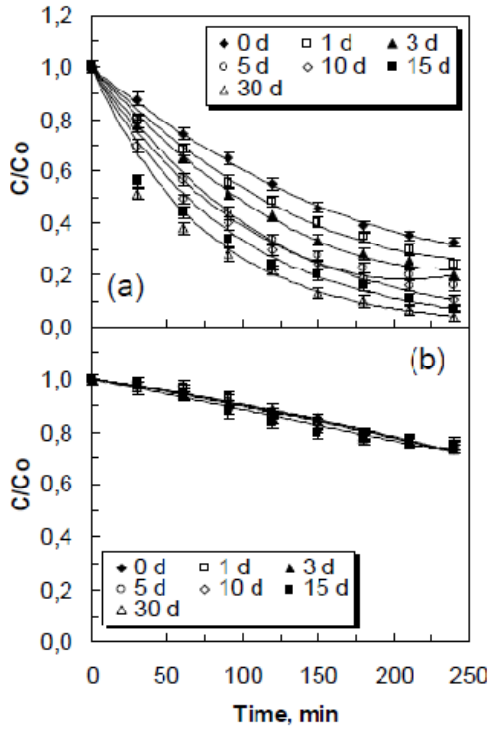

Fig. 4 Photobleaching of RB5 by ZnO thin films for different ageing times of the starting solution (0, 1, 3, 5, 10, 15 and 30 days) under (a) UV-light illumination and (b) in dark. The initial concentration of dye is 5 ppm

Figs. 4, 5 show photodegradation of the dye at different initial concentrations (5 and 20 ppm) in the presence of ZnO catalysts, deposited from starting solutions aged at different times (0, 1, 3, 5, 10, 15 and 30 day). From these graphs it can be observed a slight degradation of RB5 increasing as the aged solution increases as well. According to our results, the ZnO films with a high rough surface present a better degradation of RB5 than those with a smoother surface. The porous surface increases the active surface sites, enhancing the catalytic activity of the films, as has been established by [28]. Taking this into account, we can consider that the formation of spatial structures promote the photocatalytic activity by increasing the area exposed and enhancing the mean life of the photo-generated holes.

The same trend is followed in the three (Figs. 4 (a) and 5 (a)), that the ZnO films deposited from 30 day aged solution had highest photocatalytic activity, which was represented by largest *k* value (Fig. 6). It is interesting to note that the photobleaching of the ZnO films aged from 0 day sol was considerably lower in comparison with these prepared from 30 day sol. The proof of the experimental results is SEM images. They show that the films, which slower decolorization dye have homogenous and smooth surface. While samples with more developed surface, have better photocatalytic activity.

Photocatalytic tests conducted under irradiation with UV and visible light showed better results and higher rates of degradation of RB5 in comparison with the experiments conducted without UV irradiation (in dark). These experimentally established facts confirm photocatalytic activity of ZnO films and are presented. Experiments in the dark (Figs. 4 (b) and 5 (b)) also showed reduced concentration of Reactive Black 5, but much more slowly compared with the photocatalytic reactions for the same time. Linear fits for first order kinetics are not appropriate to describe the process. The experimental results are confirmed by the rate constants of catalytic processes. Time dependence of the decolorization efficiency of RB5 in dark is very small (Fig. 5 (b)). Nanostructured ZnO films degradation about 28% from the dye. The reduced dye concentration in this case can be due to adsorption of RB5 on the ZnO films surface. Sol-gel process usually leads to the formation of porous materials with highly developed specific surface, which may cause discoloration. However, possible destruction of a dye in the dark process conducted in the presence of films of ZnO.

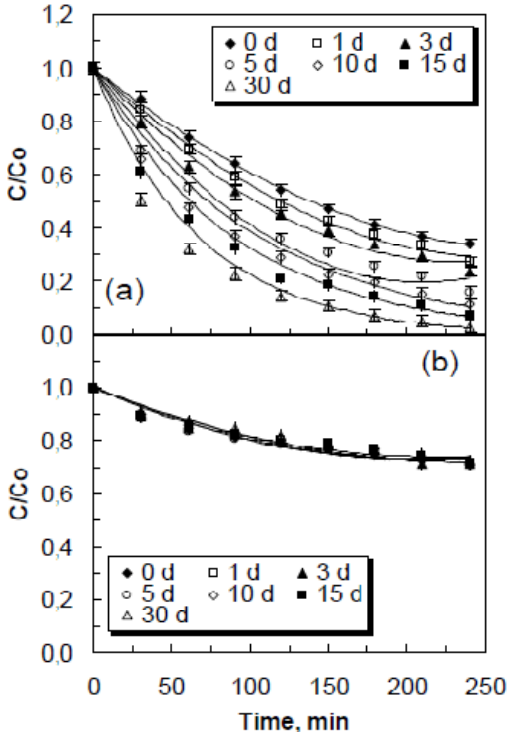

Fig. 5 Photobleaching of RB5 by ZnO thin films for different ageing times of the starting solution (0, 1, 3, 5, 10, 15 and 30 days) under (a) UV-light illumination and (b) in dark. The initial concentration of dye is 20 ppm

Nanostructured ZnO films are stability, as the photocatalytic experiments were repeated three times, using in each cycle new dye solution with the same initial concentration. All the samples were reproductives.

Fig. 6 shows the relationship between rate constants and initial concentration of the dye. The kinetics of these reactions is obtained by plotting the natural logarithm of the concentration as a function of exposure time of samples.

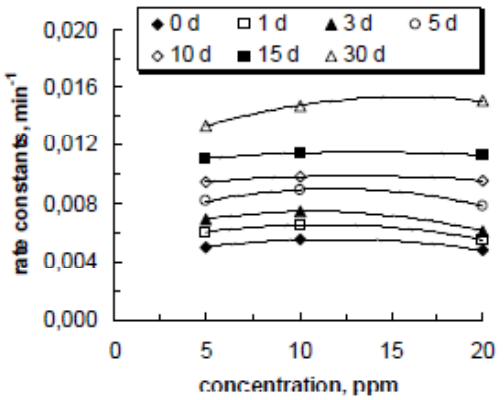

Fig. 6 Comparison of the rate constants of ZnO films at different initial concentration of the dye (5, 10 and 20 ppm) under UV-light illumination

The degradation of RB5 under UV illumination follows pseudo first-order kinetics with the slope of the logarithmic linear fits representing the reaction rate constant *k*, expressed by:

$$\ln(C/C_0) = -kt \quad (3)$$

where C_0 is the initial concentration of dye, C is the concentration of dye after irradiation in selected time interval, t and k is the rate constant.

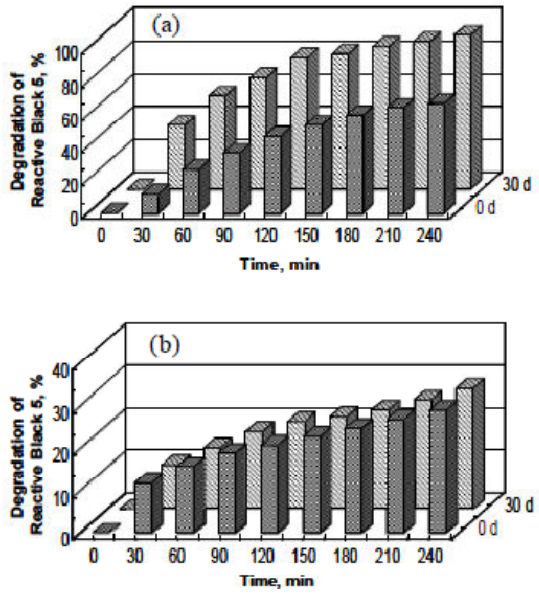

Fig. 7 Time dependence of the decolorization efficiency of RB5 aqueous solutions by ZnO films, for ageing times of the starting solution (0 and 30 days): (a) UV-light and (b) in dark. The initial concentration of dye is 20 ppm

The values of rate constants confirm the photocatalytic properties of the films. The ZnO films deposited from a 30 day aged solution have the highest photocatalytic activity under UV ($k= 0.015\ min^{-1}$) and fastest degradation the dye ($D\%= 97.22\%$, show Fig. 7 (a)). ZnO films obtained from 5 day sol have higher photocatalytic activity ($k= 0.0078\ min^{-1}$ and $D\%= 84.20\%$) than those zinc oxide films- 0 day ($k= 0.0048\ min^{-1}$ and $D\%= 65.92\%$) at initial concentration of dye 20 ppm. The calculated (using (2)) rate of dye degradation (Fig. 7) is in a good agreement with the rate constants values.

The results show that the films have significantly advanced surface are better photocatalysts. Thin films of ZnO are promising and efficient catalysts for the decomposition of organic pollutants by photocatalytic oxidation.

IV. Conclusion

Nanostructured ZnO thin films are prepared by sol–gel method and the effect of sol aging time from zinc acetate dehydrate dissolved in 2-methoxyethanol and monoethanoamine are investigated. The samples with smooth surface deposited from not stayed sol were obtained by this simple and economical method. It is possibly because the assynthesized sol is not stable enough in which the colloidal particle sizes and colloidal-particle distribution are nonuniform. As a result, the film deposited by the as-synthesized sol has relatively poor quality. With the prolonging of sol aging time, the structural and optical properties of ZnO thin films are improved gradually. The ideal aging time is suggested 30 day.

The aging time of the starting solution play an important role in the degradation performance of RB5. The photocatalysis processes show that ZnO thin films are attractive for applications in water cleaning.

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