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XPS investigation on the surface of ZnO photocatalytic films obtained by polymer modified spray pyrolysis

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Photocatalytically active ZnO nanosized films were deposited by polymer modified spray pyrolysis method. The influence of the polymers and the type of zinc precursor on the chemical composition, surface morphologies and the photocatalytic properties towards Malachite Green dye degradation were investigated. The amount of oxygen in the lattice (O_L) and oxygen total (O_T) as well as the atomic ratio of Zn/O_T were evaluated by means of X-ray Photoelectron Spectroscopy (XPS). The ZnO films are non-stoichiometric. The addition of polymers to both zinc salt solutions does not change significantly the oxygen concentration in the films. After photocatalytic test the ratio O_L/O_T decreases, showing that the amount of adsorbed hydroxyl groups is increased.

The films obtained from zinc acetate possess higher photocatalytic activity than those, obtained from zinc nitrate. The highest efficiency is achieved with the films obtained from zinc acetate with ethylcellulose addition.

Keywords: ZnO, thin films, XPS surface analysis, spray pyrolysis, photocatalytic properties

INTRODUCTION

The growth of the world's industry and population has increased the demand for water supply. The textile industries are among the industries that consume largest volumes of water in the processing operations including pre-treatment, dyeing, pattern printing and finishing. It has been reported that some of the dyes used in this industry are toxic, mutagenic and carcinogenic [1]. In general, photocatalysis is used as a pre-treating step to degrade non-biodegradable organic pollutants to biodegradable compounds. As a well-known photocatalyst, ZnO has received much attention in the degradation and complete mineralization of environmental pollutants [2].

The spray pyrolysis process, as a simple and easy thin films deposition method is one of the versatile methods to prepare thin nanosize films. The studies on the ZnO sprayed films surface by XPS analysis before and after pfotocatalysis are quite scarce in the available literature. This information is important because it elucidates the changes on the surface of the photocatalysts. Data about the effects of the polymeric modifier, added to the spray solution composition, and the nature of the zinc precursor in regard to the effectiveness of tuning of some physicochemical characteristics of the ZnO films and their correlations with the catalysts efficiency are quite a few.

In this paper we aimed at obtaining correlations between the type of polymer additive in the zinc precursor spray solution, some physicochemical characteristics and the photocatalytic properties of the ZnO films.

EXPERIMENTS

Two types of zinc precursor solutions have been prepared for the purpose of spray pyrolysis deposition. Zinc acetate ($Zn(CH_3COO)_2$) and zinc nitrate ($Zn(NO_3)_2$) were diluted in an ethanol–water mixture to obtain 0.4 M/L solutions of Zn and these were denoted as "sol A" and "sol B", respectively. The ethanol-water volume ratio in the solutions was 3:1. Polyvinyl alcohol (PVA) was prepared in ethanol-water mixture under stirring (sol C). A defined quantity of "sol C" was added to sols A or B in order to prepare the final spray solutions with 30 wt% PVA. The obtained solutions were denoted as "sol AC" and "sol BC", respectively. In parallel to this the solution of ethyl cellulose $[C_6H_7O_2(OC_2H_5)_3]_n$ in ethanol was prepared under stirring for 2h (sol D) (40wt%) and then added to "sol A" and "sol B" in order to obtain the final solutions "sol AD" and "sol BD". The aerosol was transported to the aluminum foil plates heated at

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300–400°C. Finally the films were treated at 400°C for 1h. The evaluated amount of deposited ZnO was 17 mg/cm^2.

The surface composition, type of crystalline phase and morphology have been analyzed by X-ray Photoelectron Spectroscopy (XPS), X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM). The photocatalytic experiments have been carried out using an ultraviolet light source UV-A mercury lamp. Malachite Green (MG) oxalate dye has been used as the model organic pollutant. The photocatalytic degree of degradation of 5ppm MG oxalate was measured using spectrophotometer type Jenway 6400 at regular time intervals.

RESULTS AND DISCUSSION

The XRD spectra show that all films possess a wurtzite structure and the diffraction peaks (100), (002), (101) can be indexed to hexagonal ZnO. The average crystallite sizes of the thin films are determined using the Scherrer's equation. The nitrate films possess smaller crystallite sizes (8-10 nm) in comparison to the acetate films (15-20 nm). It can be seen that in the case of nitrate the chemical nature of the zinc precursor does not influence the crystallites size. It was observed with the films, prepared from acetate solutions, that the polymer modifier PVA decreases slightly the crystallites size (10-11nm).

SEM micrographs of the zinc oxide films, prepared either from zinc acetate or from zinc nitrate solutions, exhibit different morphologies. The film, obtained by spray pyrolysis from zinc acetate, shows compact granular morphology without any visible pores and cracks, and it follows the substrates surface. It is observed that the films obtained from acetate - PVA solutions possess more developed surface with ganglia-like morphology [3] (Fig. 1b). The ethylcellulose modifier leads to highly porous morphology (Fig. 1c). The nitrate films possess fine grains with spherical shapes. In the case of nitrate solution modified with PVA or with ethylcellulose, the morphology preserves its granular character, but then it becomes more porous (Fig. 1e, f).

The surface composition and chemical state of the ZnO films have been investigated by XPS. The Zn2p spectra obtained from sol A and sol B are sharp and symmetric and have a maximum at 1021.7 eV, typical for ZnO. When polymers are added to the sols, the shape of the Zn2p peaks does not change. The binding energies of the peaks are almost the same: 1021.6 eV when PVA is used and 1021.8 eV with ethylcellulose and they are ascribed to zinc atoms in ZnO lattice. After the photocatalytic reaction, the Zn2p photoelectron peaks become wider compared to these of fresh sample (Table 1). Probably the reason for this is the formation of several phases during the photoemission. Certain quantity of ZnO formed to Zn(OH)$_2$. The deconvolution of the O1s

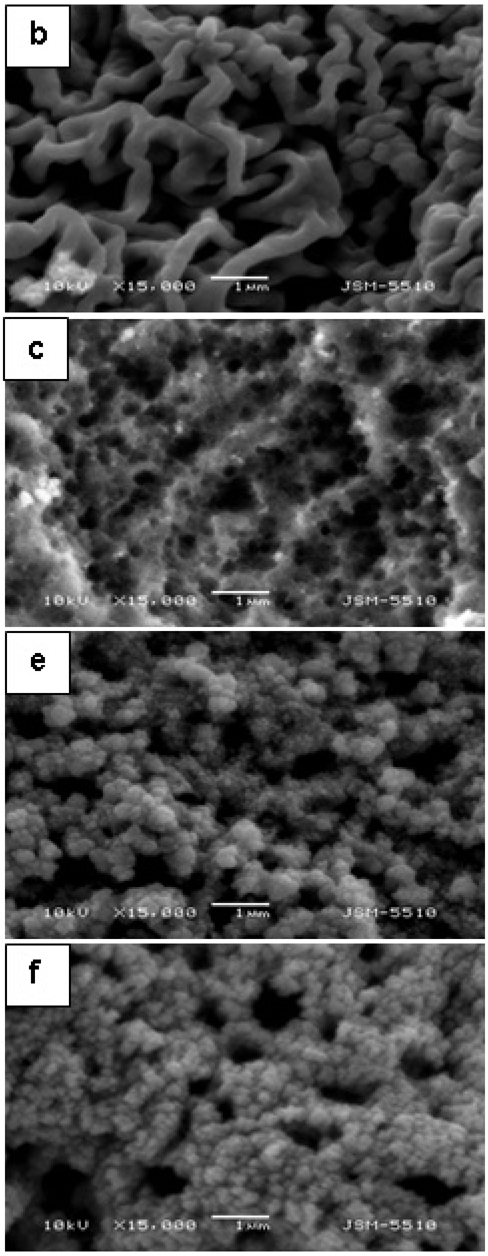

Fig. 1. SEM images on the surface of the ZnO films deposited from sol AC (b), sol AD (c), sol BC (e) and sol BD (f).

Table 1. XPS data of O and Zn elements on the surface of ZnO films

ZnO samples	Binding energy of two kinds of O1s [eV]	Atomic ratio of O_L/O_T	FWHM of $Zn2p_{3/2}$	Atomic ratio of Zn/O_L	Atomic ratio of Zn/O_T
a) sol A	530.1, 531.8	0.60	2.3	0.85	0.51
b) sol AC	530.3, 531.8	0.62	2.4	0.81	0.50
c) sol AD	530.1, 531.6	0.64	2.4	0.82	0.53
d) sol B	530.2, 531.5	0.60	2.4	0.95	0.57
e) sol BC	530.5, 532.0	0.52	2.3	1.19	0.62
f) sol BD	530.1, 531.9	0.32	2.4	1.44	0.47
b') after test	529.7, 532.0	0.21	2.9	2.05	0.43
c') after test	529.4, 531.8	0.16	3.6	1.99	0.32
ZnO powder	530.3, 531.8	0.70	2.3	1.05	0.74

O_L – crystal lattice oxygen; O_T – total oxygen

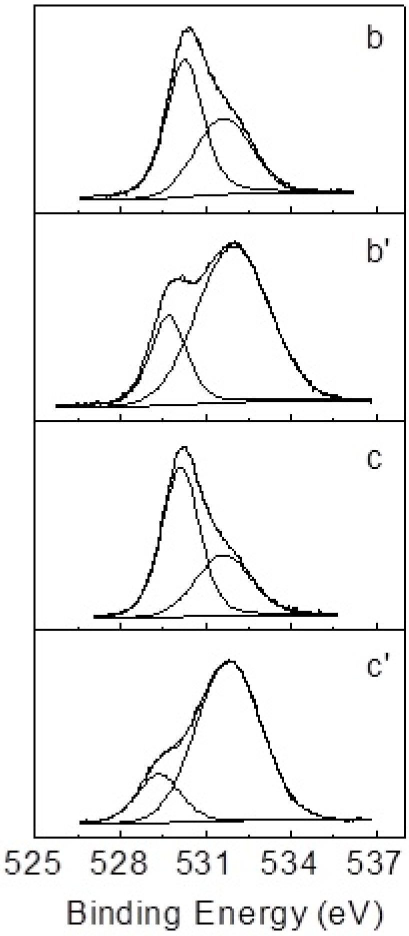

Fig. 2. O1s core level spectra of the ZnO films obtained from: sol AC (b), sol AD (c) and after photocatalysis b', c'.

photoelectron spectra of the ZnO films shows that the O1s peaks are wide and asymmetric and different oxygen states are to be distinguished. They are deconvoluted by Lorentzian–Gaussian curve fitting to two components, having the binding energy values shown in Table 1. These values are in accordance with those registered by Ayochi *et al.* for ZnO sprayed films [4]. The first component with the lower binding energy is attributed to O^{2-} ions in the ZnO lattice and the second one with the higher binding energy is ascribed to oxygen atoms in hydroxyl groups. The shape of O1s peaks for the films, prepared from unmodified and modified zinc acetate or zinc nitrate solutions, is similar. After the photocatalytic tests, the O1s photoelectron peaks showing that the amount of adsorbed OH^- groups is increased (Fig. 2). The XPS analysis indicated that the ZnO films are non-stoichiometric, which was proved by the deconvolution of the O1s peaks and the calculated Zn/O_T atomic ratio. The oxygen concentration was influenced slightly by the addition of polymers in both solutions.

Table 1 shows the XPS data of O and Zn elements on the surface of the ZnO films. It has been found out that the atomic ratios of Zn to total oxygen (O_T) for the films, obtained from different sols, are almost one and the same. This indicates that the O_T amount does not change, comparing with that of Zn. The atomic ratio of Zn to crystal lattice oxygen (O_L) for the samples, obtained from zinc nitrate, increases when polymers are added. Respectively, the amount of O_L decreases, while the amount of adsorbed OH^- species increases. In the case of pure or modified zinc acetate solutions, the atomic ratios of Zn/O_L almost do not change. The ratio Zn/O_L is higher than 1 for the polymer modified nitrate films, which could be attributed to the presence of oxygen vacancies on the surface and the formation of some more surface hydroxyl species. After photocatalytic test the ratio O_L/O_T decreases, attributed to the increased amount of hydroxyl groups at the outermost surface and adsorbed water from air moisture.

Figure 3 represents the course of dye discoloration with the time of illumination of ZnO films, using A, AC and AD solutions. The discoloration of Malachite Green dye is 73% after 3h of UV irradiation. The films prepared from unmodified solutions manifest lower activities than those of the modified films. It is probably due both to more compact structure and to slightly larger crystallites. The addition of ethyl cellulose or PVA in the solution enhances strongly the discoloration rate of Malachite Green dye. The highest photocatalytic activity is achieved with the films obtained from zinc acetate with ethylcellulose addition. The experiments showed also that the type of the zinc precursor is an important parameter for the effective discoloration of the MG. The films, obtained from zinc acetate, are more active photocatalysts than those, obtained from zinc nitrate. There are two possible explanations for this behavior: (i) the size and distribution of particle aggregates can influence both the light absorption and the light scattering mechanisms that determine the degree of photon interaction with photocatalyst surface. The scattered light intensity is probably stronger on the surface of nitrate films in comparison to the acetate films. (ii) the existence of a certain optimal value of the crystallites size; as a result below this optimal size the possibility for the electron-hole recombination increases, which is detrimental to the photocatalytic activity [5].

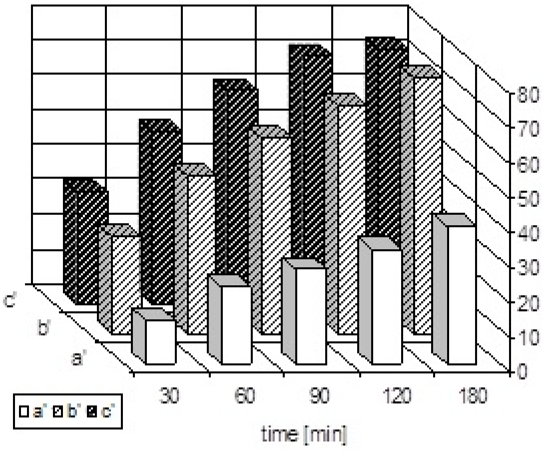

Fig. 3. Discoloration of MG with the time by ZnO films, deposited from: sol A (a'), sol AC (b') and sol AD (c').

The polymer addition to the spray solutions improve significantly the photocatalytic behavior of the films, which could be explained by changes in the morphology: from compact it becomes porous with increased surface area. The films obtained from modified zinc nitrate solutions reveal lower activity than that of the modified acetate films. The Zn/O$_L$ ratios of nitrate films are different from those of the acetate films. The Zn/O$_L$ atomic ratios for modified nitrate films are slightly higher than in the case of unmodified films, respectively the amount of O$_L$ is decreased (probably due to the formation of oxygen vacancies) (Table 1). It is known that the oxygen vacancies can trap electrons, leaving holes in the lattice. The decrease in electron density leads to an increase in the amount of the hydroxyl groups, which improve the photocatalytic activity. Salvador *et al.* [6] have also found out that the oxygen vacancies acts as effective electron scavengers for the oxidation of H_2O on the TiO_2 surface. According to the results it is obvious that in our case the films morphology affects more significantly the photocatalytic activity than the Zn/O$_L$ ratio.

CONCLUSIONS

Thin nanosize ZnO films have been prepared by polymer modified spray pyrolysis. The films morphology and the crystallites size are influenced by the nature of the zinc precursor and the presence of polymer modifier in the spray solution. The addition of polymers into spray solution leads to a more developed surface morphology and enhance significantly the photocatalytic properties of the ZnO films. According to the XPS analysis the ZnO films are non-stoichiometric, which is evidenced by the Zn/O$_T$ atomic ratio. The addition of polymers to both zinc salt solutions does not change significantly the oxygen concentration in the films. After photocatalytic test the ratio O$_L$/O$_T$ decreases, showing that the amount of adsorbed hydroxyl groups is increased.

The films obtained from ethylcellulose modified acetate solution showed the highest discoloration degree of the dye and could be promising photocatalysts for degradation of organic dyes in waste waters.

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РЕНТГЕНОВО ФОТОЕЛЕКТРОННО СПЕКТРОСКОПСКО ИЗСЛЕДВАНЕ НА ПОВЪРХНОСТТА НА ZnO ФОТОКАТАЛИТИЧНИ ФИЛМИ, ПОЛУЧЕНИ ЧРЕЗ ПОЛИМЕРНО МОДИФИЦИРАНА СПРЕЙ ПИРОЛИЗА

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(Резюме)

Фотокаталитично активни наноразмерни ZnO филми бяха отложени чрез полимерно модифицирана спрей пиролиза. Изследвани са влиянието на полимера и вида на цинковия прекурсор върху химическия състав, повърхностната морфология и фотокаталитични свойства по отношение на разграждането на малахитово зелено багрило. С рентгенова фотоелектронна спектроскопия (РФС) са изчислени количествата на кислорода в решетката (O_L) и общия кислород (O_T), както и отношението Zn/O_T. Цинково оксидните филми са нестехиометрични. Не се наблюдава значителна промяна на концентрацията на кислорода във филмите при добавянето на полимери към двата цинкови разтвора. Стойността на отношението O_L/O_T намалява след фотокаталитичния тест, което показва, че се увеличава количеството на адсорбираните на повърхността хидроксилни групи. Филмите, получени от цинков ацетат притежават по-висока фотокаталитична активност в сравнение с тези получени от цинков нитрат. Най-висока ефективност се постига с филмите, получени от цинков ацетат с етилцелулоза.