Bulgarian Chemical Communications, Volume 45, Number 2 (263 – 267) 2013

Photocatalytic degradation of malachite green by zinc oxide sprayed films

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Received January 25, 2011; revised February 19, 2012

Nanocrystalline porous ZnO films are deposited by spray pyrolysis of polyvinyl alkohol (PVA) modified zinc acetate solutions. The effect of polyvinyl alcohol on the structural, morphological and photocatalytical properties of ZnO sprayed films was studied. The X-ray diffraction patterns revealed the formation of wurtzite phase. Compact granular morphology was observed for the ZnO samples grown from zinc acetate solutions. Addition of PVA to zinc acetate leads to the formation of ganglia-like morphology. The crystallite sizes are about 10-11 nm (XRD), regardless of the type of the solvent. It was observed that PVA plays an important role in modifying the surface morphology and the photocatalytic properties of the ZnO films. The films obtained from PVA containing zinc acetate solutions showed better degradation of malachite green dye than the films deposited from solutions without polymer modifier.

Keywords: ZnO, films, photocatalysis, PVA, dye degradation

1. INTRODUCTION

Zinc oxide has been applied in solar cells [1], optoelectronic systems [2], transparent conductive oxides [3], gas sensors [4], and so forth, owing to its versatile properties. ZnO has an increasingly important status in the field of environmental protection. Zinc oxide powders and thin films are low cost and non-toxic photocatalysts for degradation of toxic organic compounds and industrial effluents under UV and visible light [5–7]. It is important to find ways for the preparation of films with porous, developed structure taking into account that the efficiency of the photocatalytic processes is attributed to the presense of more active sites.

The introduction of polymers into a zinc precursor solution can affect the films morphology and develop their surface due to a strong interfacial reaction between the inorganic metal ions and the organic polymer. This approach is mainly used in sol-gel deposition of ZnO films. Various non-ionic and polymer-type surfactants, such as polyethylene glycol (PEG) [8] and poly(vinylpyridine) (PVP) [9] were applied for preparation of nanosized ZnO films.

The spray pyrolysis offers an elegant approach to produce ZnO films with desired morphology *via* spraying a polymer-modified precursor solution. The polymer complex starts to decompose on the heated substrate and subsequent thermal treatment leads to the oxidation of the decomposition products, which ensures the formation of ZnO films with porous structure.

Recently we have successfully prepared porous sprayed ZnO films with enhanced photocatalytic activity to malachite green dye using ethylcellulose as a polymer modifier in the precursor solution [10]. It seems to be promising to proceed with the investigation in order to study the effect of other types of polymers on the structural and photocatalytic properties of ZnO films.

In this work we have chosen polyvinyl alcohol as a functional, water soluble and linear polymer, whose hydroxyl (–OH) groups at the side chains could form complexes with inorganic ions. In the process, the zinc salt was mixed with a PVA solution to issue the complex reaction between the Zn^{2+} ions and the –OH group of the PVA precursor. The cross-linking between the linear chains forms small cages which prevent the particle growth. A few investigators have used polyvinyl alcohol as a surfactant in the chemical preparation of bulk ZnO [11]. Two type of polymers (PVA and PVP) and

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zinc nitrate were used to obtain ZnO nanoparticles [12]. To our knowledge, ZnO thin films have not been prepared by spray pyrolysis using PVA additive in the precursor solution.

The aim of the present paper was to obtain photocatalytic active ZnO films with developed surface morphology using PVA-modified solution *via* simple and low cost spray pyrolysis method. The effect of the solvent on the morphological and photocatalytic characteristics was investigated.

2. EXPERIMENTAL

Zinc acetate ($Zn(CH_3COO)_2.2H_2O$) was dissolved in water or ethanol-water mixture to obtain 0.4 M/L solutions of Zn which were called *sol AcW* and *sol AcE*, respectively. To prevent the high velocity hydrolysis a few drops of HNO_3 were added to each sol. The solution of polyvinyl alcohol (PVA, Mw=40,000) in ethanol-water mixture was prepared by 5 h stirring and heating at a constant temperature of 40ºC until the final solution was clear, homogeneous, and free from precipitate (*sol C*). A defined quantity of sol C was added to the zinc acetate sols in order to obtain a final spray solution with 30 wt% PVA relative to the zinc concentration. The mixtures were vigorously stirred for 1 h and then used for the spray procedure. The alumina foil plates (80 × 25 mm) were cleaned successively in hot ethanol and acetone. The aerosol of the precursor solution was generated by a pneumatic glass nebulizer and was transported to the substrate heated at 300-400°C. Afterwards, the films were treated at 350ºC for 45 min for pyrolization of the organics and oxide formation.

The crystalline phase composition of the samples was studied by X-ray diffraction (XRD) using a X-ray diffractometer Philips PW 1050 with CuK_α-radiation. The crystallite size was estimated from the XRD spectra. X-ray diffracton line broadening (XRD-LB) measurements were carried out in order to estimate the crystallite size. Calculation was performed using Scherrer's equation:

$$D=k\lambda /B.\cos\Theta$$

where D is the crystallite size (nm), λ is the wavelength of CuK_α radiation (nm), θ is the Bragg angle (º), K is a constant (0.89) and B is the calibrated width of a diffraction peak at half-maximum intensity (rad).

The average crystallite size of the thin films is determined from the half width of full maximum (HWFM) intensity of the (100) peak. A scanning electron microscope (SEM) JSM-5510 of JEOL, operated at 10 kV of acceleration voltage was used for morphology observations of the films. The investigated samples were coated with gold by JFC-1200 fine coater (JEOL) before observation. Fourier transform infrared (FTIR) spectra were taken with a Nicolet Avatar 360 spectrometer (Nicolet, Madison, USA) spectrometer at a spectral resolution of 2 cm^{-1} and accumulation of 64 scans by the KBr tablet technique. The spectra were scanned in the 4000 – 400 cm^{-1} range. The treatment and the analysis of the spectra were made using the OMNIC advanced software.

The photocatalytic experiments were conducted using an ultraviolet source (UV lamp) with light intensity of 5.10^{-5} W/cm^2 located in the centre of a vessel. The latter contained 5 ppm aqueous solution of the dye, which was constantly agitated with a magnetic stirrer (400 rpm). The photocatalytic degradation of 5 ppm malachite green (MG) oxalate (Chroma Gesellschaft) was evaluated by taking aliquots of the solution and measuring the residual concentration on a spectrophotometer type Jenway 6400 at regular time intervals. The actual dye concentration was determined by comparison of the measured absorbance at the wavelength of the spectral maximum with the absorbance of solutions of known dye concentration.

3.RESULTS AND DISCUSSIONS

Figure 1 shows the XRD spectra of ZnO layers obtained from zinc acetate. The results show that the ZnO films obtained possess a wurtzite structure (space group P63mc) and the diffraction peaks (100), (002) and (101) can be indexed to hexagonal ZnO (JCPDS no. 36–1451). The mean size of the crystallites (calculated by Scherrer's equation) is in the range 10–20 nm.

The films obtained from $Zn(CH_3COO)_2.2H_2O$ dissolved in ethanol-water mixture (*sol AcE*) are crack-free with homogeneous, very fine grained surface (Fig 2-a). When water was used as a solvent for the zinc acetate precursor (AcW sol), the films morphology became rougher and porous, with sections of undistinguishable grain boundaries and the specimen had a net-like morphology. The crystallite sizes are slightly larger (21 nm) than those in the case of films made from AcE sol (15 nm) (Fig. 2-b). We observed significant evolution of the morphology of the samples obtained from polyvinyl alcohol-modified acetate solutions. As can be seen from Fig. 2, the addition of PVA leads to the formation of ganglia-like structure. The crystallite sizes are about 10–11 nm (XRD)

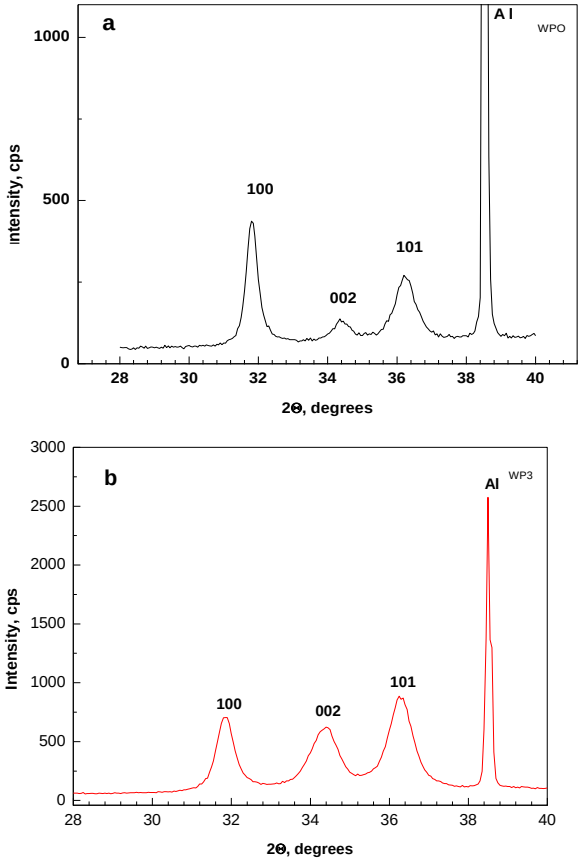

Fig 1. XRD of the films obtained from zinc acetate solution (a), PVA modified zinc acetate solution (b).

regardless of the type of the solvent. The small dimensions of the crystallite sizes could be explained taking into account the mechanism proposed in [13]. Polyvinyl alcohol adsorbs nonspecifically on the oxide surface because its molecule has no charge. It remains with a conformation similar to that of a free molecule, acting as a bridge between the particles. The cross-linking between the linear chains of PVA in aqueous medium provides small tails and loops, wherein the reactant sol is trapped and converted to small particles of ZnO during thermolysis.

It is interesting to point out that the films obtained from PVA-modified zinc acetate possess quite different morphology compared to those from the ethylcellulose-acetate solutions presented in our previous study [10]. Probably, when zinc acetate is used as a precursor for ZnO sprayed films, the nature of the added polymer modifier defines the films morphology.

The FTIR spectrum of the precursor xerogel is shown on Fig. 3. The absorption bands at 3400 and 3094 cm^{-1} (wide maximum) can be ascribed to the OH vibration stretching [14], the bands at 2929 and 2856 cm^{-1} are attributed to CH and CH_2 vibration

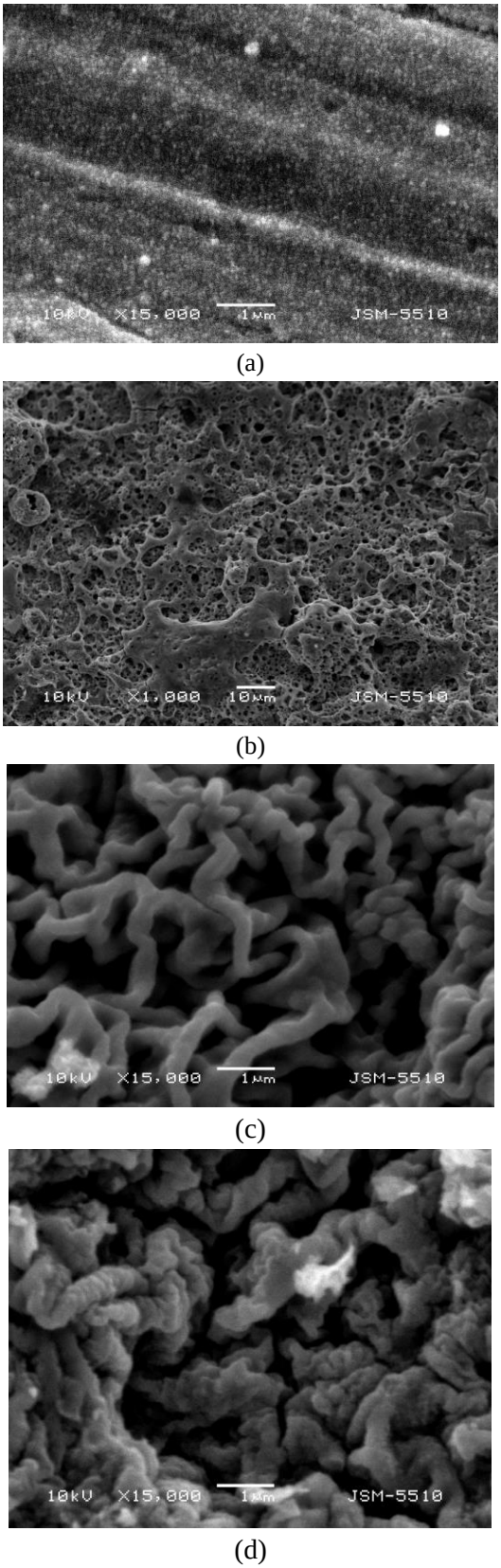

Fig 2. SEM of ZnO films deposited from ethanol-water solution (a), from aqueous solution (b), from PVA modified ethanol-water solution (c), PVA modified aqueous solution (d).

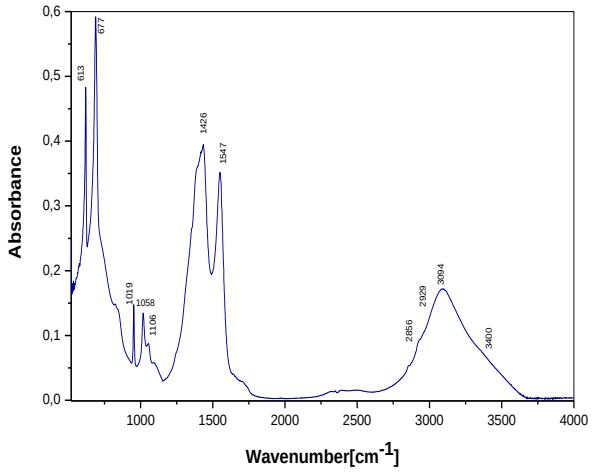

Fig 3. Fourrier transform infrared (FTIR) spectra of ZnO precursor solution with PVA modifier, dried at 80°C.

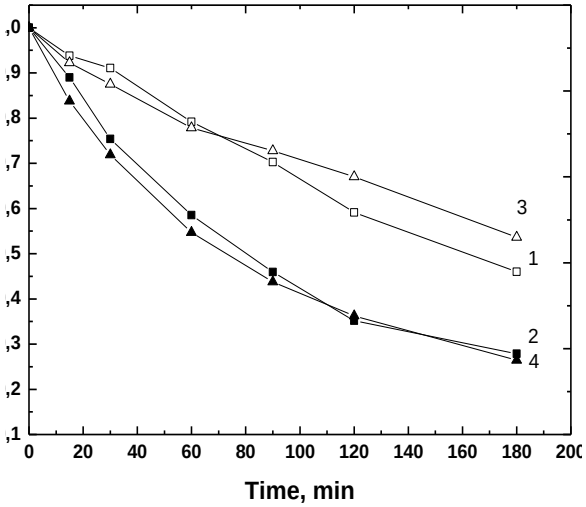

Fig.4. Photocatalytic degradation of Malachite Green on ZnO films deposited from:-AcW solution - curve1; PVA modified AcW solution-curve 2; AcE solution –curve 3 and PVA modified AcE solution of $Zn(CH_3COO)_2.2H_2O$ - curve 4.

stretching and are typical of PVA [15,16]. The band at 1714 cm^{-1} is characteristic of C=O and C–O stretching [17]; the intensive bands at 1547 and 1426 cm^{-1} are also related with C=O and C-O stretching, where the peak at 1547 cm^{-1} can be assigned to C=O bridging type metal acetate bonding. Both bands are characteristic of zinc acetate [18,19]. The bands in the range 950-1110 cm^{-1} are identified as CH_3 bending modes [14]. The stretching at 842 cm^{-1} can be referred to CH_2 and is characteristic of PVA [35]. The latter two bands at 677 and 613 cm^{-1} belong to zinc acetate [14].

The photocatalytic activity of the obtained films was evaluated under illumination with UV light. The change of the relative concentration C/C_o (where C_o is the initial concentration of MG) of the dye on ZnO films deposited from $Zn(CH_3COO)_2.2H_2O$ (*sols AcW, AcE*) with and without PVA addition with the time of UV radiation is shown in Fig. 4. As can be seen on the figure, the addition of PVA in the spray solution of zinc acetate strongly enhances the degradation rate of the malachite green dye (curves 2,4 *vs* curves 1,3). Curves 2 and 4 show a similar course of photocatalytic degradation for both modified sprayed ZnO films. Malachite green dye undergoes 50 % decomposition within 1 hour of UV irradiation. One can conclude that the enhancement in the photocatalytic activities can be attributed to the well developed structure of the films obtained by PVA modified AcE and AcW solutions, which ensures a larger amount of active sites for the photocatalytic process.

The films obtained from unmodified solutions possess lower activities probably due to both the more compact structure and the slightly larger crystallites (Fig. 4, curves 1,3). The best photocatalytic activity is achieved for the films obtained from PVA-modified ethanol-water solutions of zinc acetate.

4. CONCLUSIONS

Nanosized thin ZnO films were prepared by spray pyrolysis from polyvinyl alcohol modified solutions. The films obtained form zinc acetate solutions have relatively compact structure with crystallite size of 15–20 nm. The addition of PVA leads to a smaller crystallite size (about 10–11 nm), regardless of the type of the solvent and ganglia-like structure. The well developed surface structure with fine grains determines the better photocatalytic properties of the films from polymer-modified solutions.

Acknowledgements: *The financial support by the Bulgarian Ministry of Education and Science (Project TK-X-1702/07) is greatly acknowledged.*

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ФОТОКАТАЛИТИЧНО РАЗГРАЖДАНЕ НА МАЛАХИТОВО ЗЕЛЕНО ЧРЕЗ СПРЕЙВАНИ СЛОЕВЕ ОТ ZnO

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Постъпила на 25 януари, 2011 г.; коригирана на 19 февруари, 2012 г.

(Резюме)

Нанокристални порести филми от ZnO бяха отложени чрез спрей пиролиза на модифициран с поливинилов алкохол (PVA) разтвор на цинков ацетат. Изследван е ефектът на поливиниловия алкохол върху структурните, морфологични и фотокаталитични свойства на спрейвани филми от ZnO. Рентгеновата дифракция разкри образуването на чиста вюрцитна фаза. Наблюдавана е компактна гранулирана морфология за слоевете от ZnO, получени от цинков ацетат. Добавянето на поливинилов алкохол към цинков ацетат води до формиране на ганглии. Размерите на кристалитите са около 10-11 нанометра (XRD), независимо от вида на разтворителя. Беше установено, че PVA играе важна роля в промяната на морфологията и на фотокаталитичните свойства на филмите от ZnO. Слоевете, получени от модифицирани с поливинилов алкохол разтвори на цинков ацетат, провяват по-висока активност за разграждане на багрилото малахитово зелено, отколкото филмите, отложени от разтвор без полимерен модификатор.