



Photocatalytic zinc oxide thin films obtained by surfactant assisted spray pyrolysis deposition



M. Duta^{a,b}, D. Perniu^a, A. Duta^{a,*}

^a Research Centre: Renewable Energy Systems and Recycling, Transilvania University, Eroilor 29, 500036 Brasov, Romania

^b "Ilie Murgulescu" Institute of Physical Chemistry of the Romanian Academy, Bucharest, Romania

ARTICLE INFO

Article history:

Received 7 December 2013

Received in revised form 6 February 2014

Accepted 22 February 2014

Available online 1 March 2014

Keywords:

ZnO

Thin film

Surfactant

Spray pyrolysis deposition

Photocatalysis

ABSTRACT

Zinc oxide thin films were obtained by spray pyrolysis deposition using three surfactants with linear C₁₂ tails as soft templating agents: anionic sodium dodecylsulfate (SDS), cationic dodecyltrimethylammonium bromide (DTAB) and nonionic dodecanol (DD). The influence of the surfactants' type and concentration (above and below critical micelle concentration in the precursor system) on the thin film formation was investigated and was correlated with their photocatalytic efficiency in methylorange removal, under visible and UV irradiation. The surfactants influence both the nucleation and growth stages, mainly through the Zn-surfactant interactions at the droplet border and/or on the micelles. *In situ* doping with Na⁺ (in SDS) improves the removal efficiency up to 19.88% under VIS irradiation, while the highest removal efficiencies in ZnO thin films obtained using DTAB and DD are 16.27% and 15.44%, respectively. Under UV irradiation the highest efficiencies are 45.28% (SDS), 51.59% (DTAB) and 49.43% (DD).

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Zinc oxide is a wide band gap semiconductor ($E_g = 3.37$ eV) with large exciton binding energy and good optical, piezoelectric and pyro-electric properties; therefore ZnO applications range from optoelectronics (solar cells, lasers, photodiodes) up to chemical and biological sensors or electro-acoustic transducers [1–4]; lately ZnO was reported to be efficient also as photocatalyst in wastewater treatment [3,4], this application being supported by its lack of toxicity.

There are many physical and chemical methods for obtaining ZnO films: molecular beam epitaxy, pulse laser ablation, sputtering, chemical vapour deposition, self-assembly of diblock copolymer, sol-gel, electrochemical deposition, chemical bath, etc. Among these, spray pyrolysis deposition (SPD) [5–7], is simple, up-scalable, able to use inorganic precursors thus relatively non-toxic, and offers good control over the deposition parameters. For tuning the thin film properties, additives as alcohols, chelating agents or surfactants can be used, the latest mainly acting as growth controlling agents (soft templating agents) and agglomeration inhibitors [8–11]. Interactions with the precursor can vary depending on the surfactant head (anionic, cationic or non-ionic), hydrocarbon tail

(length, ramification, other atomic species) and, in a less extent, on the counter-ions. These interactions lead to new ordering at the interface and/or inside the precursor systems and can be further controlled through the solvent composition, with consequences on the crystallinity, morphology and wetting ability of the thin films, according to the surfactant concentration, correlated to the critical micelle concentration (CMC), as the potential templating effect could be significantly different before and after micelles' formation.

Studies of ZnO electrodeposition with surfactants were reported using sodium dodecyl sulfate (SDS) [12–14] and alkylphenol polyoxyethylene (10) ether [15] while the cationic cetyl trimethylammonium bromide (CTAB) was reported to offer good morphological control of ZnO thin films obtained by hydrothermal process [16–18]. A comparative study on the effect of SDS, CTAB and nonionic (hexamethylenetetramine) was also reported in a room temperature chemical precipitation of ZnO [19], confirming different growth mechanisms depending on the surfactant's charge/polarity.

Lately ZnO obtained by SPD was reported [20], including results on systems also containing poly(vinyl alcohol) as templating agent [21]. But, to the best of our knowledge there are not studies analyzing the effect of surfactants in the pre-micellar systems and above CMC, reporting on ZnO obtained by SPD for tailoring the photocatalytic properties.

This paper investigates the templating effect of a series of surfactants with C₁₂ linear hydrocarbon tail on the ZnO thin films

* Corresponding author. Tel.: +40 723561089.

E-mail address: a.duta@unitbv.ro (A. Duta).

Table 1

Critical micelle concentrations in water and in the precursor system, and experimental concentrations of the surfactants in the precursor systems used to obtain ZnO thin films.

Surfactant	SDS	DTAB	DD
CMC in water (ppm)	2307 [22]	4347 [23]	Non-soluble
CMC in the precursor solution (ppm)	96	362	820
Experimental Concentration below CMC (ppm)	50	200	500
Sample label	SDS 50	DTAB 200	DD 500
Experimental Concentration above CMC (ppm)	150	600	1000
Sample label	SDS 150	DTAB 600	DD 1000

deposited by spray pyrolysis deposition. The pristine ZnO deposition conditions were initially optimised and were further used in all experiments; the substrate temperature was $T = 250^\circ\text{C}$, and air was used as carrier gas, at 1.5 bars. The spraying parameters were: spraying angle 45° ; nozzle–substrate distance 23 cm; number of spraying sequences: 20, with 20 s break. An anionic (sodium dodecylsulfate, SDS), a cationic (dodecyltrimethylammonium bromide, DTAB) and a non-ionic (dodecanol, DD) surfactant are selected and experiments are developed in precursors systems at concentrations below and above CMC; the influence of the surfactant type (head) and concentration on the structural, morphological and electric properties of zinc oxide thin films is investigated and is correlated with the efficiency of the photocatalytic degradation of methylo-range.

2. Experimental

2.1. Thin film deposition

The following materials were used for obtaining the thin ZnO films:

Substrate: 2.5 cm \times 2.5 cm fluorine-doped tin oxide substrates (FTO Pilkington TEC 15). The FTO substrates were cleaned with water and pH neutral detergent followed by ultra-sonication in ethanol for 5 min and drying in compressed air.

Zinc precursor: $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (Scharlau 99.5%); in all experiments $c_{\text{Zn}} = 0.15\text{ M}$.

Solvent: Water–ethanol (PAM Corporation 99.2%) mixed solvent, molar ratio 1:1.

Additives: 0.5 mL acetyl acetone (Alfa Aesar 99%) was added in the precursor solution as morphology control agent for increasing homogeneity ($V_{\text{AcAc}} : V_{\text{Zn}^{2+}, \text{solution}} = 1 : 100$). Additionally, different volumes of C_{12} surfactants: SDS (Sigma–Aldrich 98.5%), DTAB (Sigma 98%), DD (Alfa Aesar 98%) were added at concentrations below and above CMC.

2.2. Thin film characterization

The CMC was experimentally evaluated based on conductivity measurements (Hanna Instruments HI 8424 conductometer), at the breaking point on the curve which describes the concentration dependence of conductivity and the results are presented in Table 1; further experiments were done in systems with the surfactant concentrations below and above CMC.

For comparison reasons, Table 1 also includes literature CMC data for the aqueous surfactants systems.

The crystallinity of the zinc oxide thin films was investigated using a Bruker D8 Discover X-ray diffractometer ($\text{Cu}_{\text{K}\alpha 1} = 1.5406\text{ \AA}$, locked-couple technique, step size 0.035, scan speed 2 s/step, 2θ range from 20 to 70°).

The band gap energy and film thickness were evaluated based on the transmittance and reflectance spectra, using a UV–vis–NIR spectrophotometer (Perkin Elmer Lambda 950).

Scanning electron microscopy was used to investigate the thin films' surface using a Hitachi SEM S-3400M apparatus coupled with a Thermo ScientificUltraDry 4481B–1UES–SN energy dispersive X-ray spectrometer (EDS).

Atomic force microscopy (NT-MDT model NTGRA PRIMA EC, semicontact mode with Si-tips, NSG10, force constant 0.15 N/m, tip radius 10 nm) was used for surface topography studies. Roughness was calculated using the AFM software for the $20\text{ }\mu\text{m} \times 20\text{ }\mu\text{m}$ surface (acceptable error $\pm 0.1\text{ nm}$).

The contact angle (θ) measurements on the thin films was done using the sessile drop method, at room temperature (20°C) using the OCA-20 Contact Angle-meter (DataPhysics Instruments). Two testing liquids with different polarity and surface tension ($\sigma_{\text{L,V}}$) were used: glycerol ($\sigma_{\text{L,V}}^{20^\circ\text{C}} = 63.40\text{ mN/m}$) and deionized water ($\sigma_{\text{L,V}}^{20^\circ\text{C}} = 72.80\text{ mN/m}$).

2.3. Photocatalysis experiments

Photodegradation tests were carried out in a reactor containing three UV light sources (UVA light, typically 340–400 nm, $\lambda_{\text{max}} = 365\text{ nm}$); the black light tubes were replaced for VIS experiments (VIS light, 18 W/865). Methylorange (MO, Merk, reagent grade) was used as reference pollutant in previously optimized process conditions [24]; the thin films were immersed in 25 mL of methylorange solutions (0.0125 mM) to which H_2O_2 was added (3 mL/L of dye solution) as electron acceptor. All the tests were run at the natural pH of the solutions (pH 5.2–5.4). Before starting the photocatalytic tests, the samples were left 30 min. in dark to reach the adsorption equilibrium.

The photodegradation efficiency, η , was calculated based on the initial absorbance of the dye solution (A_0) and the absorbance after 360 min (A), recorded at the maximum absorbance wavelength for methylorange ($\lambda = 463\text{ nm}$), using Eq. (1):

$$\eta = \frac{A_0 - A}{A_0} \times 100 \quad (1)$$

3. Results and discussion

3.1. Structural characterization of zinc oxide thin films

The XRD spectra in Fig. 1 indicate that wurtzite represents the crystalline phase in each film. The tin oxide peaks can be attributed to the substrate and suggests that films with low thickness are obtained.

Based on the values of the full width at the half maximum (FWHM) of the representative (1, 0, 0) peak, the crystallite sizes (D) and the microstrains (ε) were calculated, using the Scherrer (Eq. (2)) and the Wilson (Eq. (3)) formulae, and the data are presented in Table 2:

$$D = \frac{0.9\lambda}{\text{FWHM} \cos \theta} \quad (2)$$

$$\varepsilon = \frac{\text{FWHM}}{4 \tan \theta} \quad (3)$$

Download English Version:

<https://daneshyari.com/en/article/5358712>

Download Persian Version:

<https://daneshyari.com/article/5358712>

[Daneshyari.com](https://daneshyari.com)