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

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A R T I C L E   I N F O

Article history:
Received 7 December 2013
Received in revised form 6 February 2014
Accepted 22 February 2014
Available online xxx

Keywords:
ZnO
Thin film
Surfactant
Spray pyrolysis deposition
Photocatalysis

A B S T R A C T

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 dodecytrimethylammonium 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 methylene blue 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).

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1. Introduction

Zinc oxide is a wide band gap semiconductor (Eg = 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.
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.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>SDS</th>
<th>DTAB</th>
<th>DD</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMC in water (ppm)</td>
<td>2307</td>
<td>4347</td>
<td>Non-soluble</td>
</tr>
<tr>
<td>CMC in the precursor solution (ppm)</td>
<td>96</td>
<td>362</td>
<td>820</td>
</tr>
<tr>
<td>Experimental Concentration below CMC (ppm)</td>
<td>50</td>
<td>200</td>
<td>500</td>
</tr>
<tr>
<td>Sample label: SDS 50</td>
<td>DTAB 200</td>
<td>DD 500</td>
<td></td>
</tr>
<tr>
<td>Experimental Concentration above CMC (ppm)</td>
<td>150</td>
<td>600</td>
<td>1000</td>
</tr>
<tr>
<td>Sample label: SDS 150</td>
<td>DTAB 600</td>
<td>DD 1000</td>
<td></td>
</tr>
</tbody>
</table>

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 °C, and air was used as carrier gas, at 1.5 bars. The spraying parameters were: spraying angle 45 °C; 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 precursor 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 methylene blue.

2. Experimental

2.1. Thin film deposition

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

**Substrate:** 2.5 cm × 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:** Zn(CH3COO)2 · 2H2O (Scharlau 99.5%); in all experiments Czno = 0.15 M.

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

**Additives:** 0.5 M acetyl acetone (Alfa Aesar 99%) was added in the precursor solution as morphology control agent for increasing homogeneity (VAc : VZn(CH3COO)2 · 2H2O : solution = 1 : 100). Additionally, different volumes of C12 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 surfactant systems.

The crystallinity of the zinc oxide thin films was investigated using a Bruker D8 Discover X-ray diffractometer (CuKα1 = 1.5406 Å, 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 Scientifc Ultra Dry 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 μm × 20 μm surface (acceptable error ±0.1 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 (σLV) were used: glycerol (σLV = 63.40 mN/m) and deionized water (σLV = 72.80 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, λmax = 365 nm); the black light tubes were replaced for VIS experiments (VIS light, 18 W/865). Methylene blue (MO, Merk, reagent grade) was used as reference pollutant in previously optimized process conditions [24]; the thin films were immersed in 25 mL of methylene blue solutions (0.0125 mM) to which H2O2 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 (A0) and the absorbance after 360 min (A), recorded at the maximum absorbance wavelength for methylene blue (λ = 463 nm), using Eq. (1):

\[
\eta = \frac{A_0 - A}{A_0} \times 100
\]

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:

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

\[
\varepsilon = \frac{\text{FWHM}}{4\tan \theta} \quad (3)
\]
A comparative analysis of the crystallite sizes shows that the surfactant type has a significant influence on the film-formation process. Thus, the largest crystallites correspond to the most stabilized zinc intermediate (obtained using SDS) and the lowest to the systems containing DTAB, as result of the weaker interactions. As expected, these structures, with lower crystallinity and higher disorder show the largest microstrains and indicate a more random growth.

The layer thickness is influenced by the critical micelle concentration (with thicker films at concentrations below CMC), Table 3. In this case, the Zn–AcAc–Surfactant structures will be formed and will start to react close to the droplet surface; afterwards, most of the template/surfactant is subject to thermal decomposition, leaving porous, regular structures. The pristine sample has a comparable thickness to that of the SDS 150 sample, suggesting that the reactivity of the Zn–AcAc structure is comparable to that of the SDS–Zn–AcAc compounds. The largest thickness, for films obtained using DD can be correlated with the large amount of surfactant in the system (as DD has the largest CMC value, the experimental DD concentrations were rather high); these can lead to a significant amount of by-products trapped in the film, thus thicker films due to a weight increase.

The band gap energy was investigated based on the transmission spectra (Fig. 2) and the values are presented in Table 3. The band gap of the pristine sample is 3.28 eV and is comparable to the value reported for bulk zinc oxide (3.3 eV [1]). Significantly higher band gap values are characterising the films obtained using surfactants, and these values are not respecting the trend imposed by the crystallites sizes, therefore one can conclude that this is the result of additional by-products resulted in the pyrolysis process of the surfactants. These by-products can be carbon based (and this can be correlated with the amount of surfactant) or are possible doping species, from the ionic surfactants’ molecules (sulfur, nitrogen or Br– and Na+). When using DD, only carbonaceous by-products can be expected; as the band gap values show, their contribution is almost constant, regardless the surfactant’s concentration. A more significant increase in the band gap energy is registered in the sample containing SDS bellow CMC; this could be correlated with the doping effect of the Na+ cations, developing oxygen vacancies that, in rich oxygen atmosphere, are passivated and increase the amount of holes. This effect is less obvious at concentrations above CMC and can indicate different stabilizing mechanisms, when interstitial sodium can also be expected in the lattice.

The transmission spectra show that the films are transparent in the VIS spectral region, Fig. 2, with transmittance values between 85 and 98% and slight modulation, mainly as result of the films porosity. The highest transmittance corresponds to the thin, smooth films obtained using SDS. On the other hand, these films show the highest reflectance (R=18%) (Fig. 3). The lowest

---

**Table 2**

Crystallite sizes in the ZnO pristine sample and in the thin films obtained using surfactant additives.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pristine</th>
<th>SDS 50</th>
<th>SDS 150</th>
<th>DTAB 200</th>
<th>DTAB 600</th>
<th>DD 500</th>
<th>DD 1000</th>
</tr>
</thead>
<tbody>
<tr>
<td>r</td>
<td>0.00909</td>
<td>0.00949</td>
<td>0.01005</td>
<td>0.01256</td>
<td>0.01508</td>
<td>0.01106</td>
<td>0.01135</td>
</tr>
<tr>
<td>FWHM</td>
<td>0.594</td>
<td>0.520</td>
<td>0.654</td>
<td>0.830</td>
<td>0.987</td>
<td>0.723</td>
<td>0.772</td>
</tr>
<tr>
<td>θ [°]</td>
<td>15.917</td>
<td>15.916</td>
<td>15.845</td>
<td>15.940</td>
<td>15.940</td>
<td>15.926</td>
<td>15.967</td>
</tr>
</tbody>
</table>

**Table 3**

Band gap energies and film thickness of zinc oxide thin films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pristine</th>
<th>SDS 50</th>
<th>SDS 150</th>
<th>DTAB 200</th>
<th>DTAB 600</th>
<th>DD 500</th>
<th>DD 1000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eg [eV]</td>
<td>3.28</td>
<td>3.76</td>
<td>3.49</td>
<td>3.49</td>
<td>3.47</td>
<td>3.40</td>
<td>3.38</td>
</tr>
<tr>
<td>d [nm]</td>
<td>372</td>
<td>424</td>
<td>379</td>
<td>445</td>
<td>362</td>
<td>675</td>
<td>561</td>
</tr>
</tbody>
</table>

---

![Fig. 1](image1.png)

**Fig. 1.** XRD patterns of ZnO thin films obtained without (pristine) and with surfactant addition.

![Fig. 2](image2.png)

**Fig. 2.** Transmittance spectra (a) and Tauc plots (b) for the ZnO thin films.

Please cite this article in press as: M. Duta, et al., Photocatalytic zinc oxide thin films obtained by surfactant assisted spray pyrolysis deposition, Appl. Surf. Sci. (2014), [http://dx.doi.org/10.1016/j.apsusc.2014.02.132](http://dx.doi.org/10.1016/j.apsusc.2014.02.132)
reflectance corresponds to the film obtained using DTAB,600 which also has the highest roughness, supporting multiple inside reflections, with a possible positive effect on the photogeneration efficiency.

In order to give evidence on the possible by-products in the films, surface elemental analysis of the films was done using EDS. Based on the results, a qualitative estimation showed that carbon based compounds (e.g. carboxylate, carbonyl) are trapped in the film, resulted from incomplete decomposition of the precursor, surfactant or AcAc (as the pristine sample also contains carbon). On the analysed spots, the carbon range from 5.17% (in the pristine sample) up to 11.89% for the sample obtained using DD. The sulphur trapped in the SDS,150 sample (amounting less than 0.2%) indicates the incomplete decomposition of the surfactant into volatile compounds when SDS is in larger amount. Tin and silicon are also identifiable from the substrate, due to the low thickness of the films.

3.2. Surface characterization of the zinc oxide thin films

Through SEM analysis (Fig. 4) zinc oxide films were observed containing nanowires aggregated in 2D coherent structures grown on regular 3D beds. A common trend for all the thin films is the dendritic type of structures as result of a step-wise development of the nucleation sites with increasing the number of spraying sequences. This can explain the two types of morphologies, suggesting that the homogenous bed is a result of the timely growth and overlapping of the nanowire structures. The shape of the nanowire structures can be correlated with the crystal growth mechanism which is preferentially initiated from the most active sites (edges and corners) [25] and runs fast for the less stable reactants; as result, the DTAB-Zn-AcAc lower stability structures will have increased growth rate leading to the formation of fragile, larger nanowires (nanoribbons) which can crumble (Fig. 4e). One may conclude that this rapid growth is difficult to control, as already indicated by the XRD data, leading to lower crystallinity. For the more stable Zn-AcAc (in the pristine sample) and Zn-SDS compounds, nucleation is slower, the active sites are fewer and so are the 2D structures. The pristine sample and the ones with SDS are morphologically similar, and substantially differ from those with DTAB and DD, suggesting that the attractive interaction represents an important factor also in the film growth mechanism along with the amount of surfactant.

The samples with concentration below and above CMC have quite similar surface aspect for each surfactant, confirming the SEM findings and showing that the type of surfactant is more important than its concentration. Atomic force microscopy analysis was performed on the zinc oxide thin films and the results are presented in Fig. 5.

The average film thickness and the skewness factor were calculated using the AFM software and are presented in Table 4. The results show that surfactants addition leads to lower average roughness as compared to the pristine sample, confirming their ordering/templating effect at mezzo- and micro-level. For systems where weak or repulsive interactions are expected (containing DD or DTAB), roughness increases with the surfactant concentration supporting the previous assumptions of more random growth. The system that contains SDS above CMC leads to films with the lowest roughness, confirming the ordering effect based on attraction forces.

The skewness factor (Table 4) shows that film morphology predominantly consists of peaks, with only one sample with negative Ssk (DD,500), corresponding to a porous surface. However, values remain below unit, indicating an overall smooth morphology.

These data outline various interactions involving the zinc precursor, the surfactants and the other ionic species in the precursor system.

In aqueous media, the zinc cation is hydrated. By adding ethanol (as co-solvent) the water molecules can be partially replaced by ethanol molecules, while acetylacetone addition can involve the metal cation in complex-type structures; all these new species allow controlling the cation precursor stability, thus the nucleation rate. These types of interactions can occur in the entire volume of the precursor system. Surfactants included in this system will firstly occupy the liquid/air interface (below CMC) and will further form micelles at concentrations above CMC. The templating effect of surfactants is mainly the result of electrostatic attractions, as presented in Scheme 1.

The strongest ordering effect is expected in direct zinc cation–anionic surfactant interactions and the lower roughness of the films obtained using SDS in the micelle-containing systems confirm this mechanism. Direct attractive interactions between the cationic DTAB and the zinc cation species can occur only via a double layer developed by the anions in the precursor system (i.e. Br− from DTAB or CH3COO− from the zinc precursor), therefore the ordering effect is lower and the films are growing more random, with higher roughness and lower crystallites. The decrease in the templating effect is stronger when DTAB micelles are formed and are mirrored in the morphology. The non-ionic DD will promote weaker interactions, both with the cations and anions, supporting faster growth and high roughness films.

These structures formed in the precursor system will be found in the aerosol cone during spraying. While approaching the heated substrate, the droplets will be heated, the solvent(s) will evaporated and the ionic concentration will increase in the shrinking volume of the droplet. These physical processes are complementary with the chemical reactions, as the confined space and the templating effect will support higher local concentrations, thus the beginning of nucleation. The morphology data show that this process is more likely when using the cationic and non-ionic surfactants and can be the result of the significantly larger DTAB and DD micelles, as compared to SDS (according to the CMC values).

The combined effect of surfactant addition on the films crystallinity and morphology will further influence the properties with direct influence on the photocatalytic process: the wettability and the process efficiency.

The surface energy and wetting behaviour of the thin films is important in photocatalysis as the main mechanism involves water interaction. The surface energy and its dispersive and polar components were evaluated based on the contact angle measurements.

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Fig. 5. AFM images of (a) pristine ZnO, (b) SDS 50, (c) SDS 150, (d) DTAB 200, (e) DTAB 600, (f) DD 500 and (g) DD 1000.
of distilled water and glycerol, using the Owens–Wendt–Rabel and Kaelble equation [26]:

\[
\frac{(1 + \cos \theta) \cdot \sigma_L}{2 \sqrt{\sigma_L^2}} = \sqrt{\sigma_S^P \cdot \sigma_L^P} + \sqrt{\sigma_S^D \cdot \sigma_L^D}
\]  

(4)

where \(\sigma_L^P\) and \(\sigma_L^P\) represent the dispersive and polar components of the liquid, \(\sigma_S^P\) and \(\sigma_S^D\) represent the respective contributions of the solid and \(\theta\) is the contact angle of the testing liquids on the substrates [27].

The results are presented in Table 5 and indicate predominant polar/charged surfaces. The data show that, although with lower roughness compared to the pristine ZnO, the samples obtained with surfactant addition have higher surface energy (especially significant lower contact angles with water).

Another important feature of the photocatalysts is the hydrophilic behaviour that allows good wetting and supports the adsorption of charged pollutants. The contact angles values measured using water are lower for all the films obtained using surfactants, as compared to the pristine sample. Small variations induced by concentration are observed in the contact angle values for the samples obtained using the negatively charged molecules of SDS and DD, while a significant increase in hydrophilicity is registered when using the positively charged DTAB, at the concentration above CMC. A complex of factors is responsible for this behaviour: surface composition (specifically by-products), morphology and crystallinity; considering the large values of the polar component in the surface energy, one may conclude that surface composition plays an important role. The surface morphology is also important, as large surface energy corresponds to the films with the largest surface roughness (samples DTAB_600 and DD_1000). Both, composition and morphology are influenced by the different interactions between the zinc cation and the surfactants (Scheme 1).

### 3.3. Photocatalysis efficiency

Based on the previous results, the ZnO films were investigated for photocatalytic applications in wastewater treatment, using methylene blue as reference dye. The band gap values calculated for the thin films (Table 3) show that ZnO activity would need UV-activation. Still, as the data show, residual compounds are also trapped within the films and UV-activity is possible. The bleaching efficiency was investigated in two series of experiments, and the results obtained under UV and under VIS irradiation are presented in Table 6.

As expected, the best photodegradation efficiencies are obtained under UV light, with comparable results for all samples. It is to mention that preliminary UV–VIS and FTIR spectra of the dye solution do not show any supplementary peaks after photocatalysis.

### Table 5

Contact angle and surface energy values for ZnO thin films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Contact angle (\theta) (°)</th>
<th>SE (mN/m)</th>
<th>(\sigma_L^P) (mN/m)</th>
<th>(\sigma_L^D) (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Water</td>
<td>Glycerol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pristine</td>
<td>67.79</td>
<td>63.89</td>
<td>71.02</td>
<td>0.57</td>
</tr>
<tr>
<td>SDS_50</td>
<td>40.99</td>
<td>62.77</td>
<td>78.95</td>
<td>0.01</td>
</tr>
<tr>
<td>SDS_150</td>
<td>42.20</td>
<td>60.81</td>
<td>72.59</td>
<td>0.33</td>
</tr>
<tr>
<td>DTAB_200</td>
<td>40.06</td>
<td>56.68</td>
<td>76.12</td>
<td>1.12</td>
</tr>
<tr>
<td>DTAB_600</td>
<td>26.87</td>
<td>57.14</td>
<td>96.09</td>
<td>0.06</td>
</tr>
<tr>
<td>DD_500</td>
<td>46.34</td>
<td>68.66</td>
<td>78.71</td>
<td>0.14</td>
</tr>
<tr>
<td>DD_1000</td>
<td>43.22</td>
<td>68.35</td>
<td>86.27</td>
<td>0.48</td>
</tr>
</tbody>
</table>

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Table 6: Photocatalysis efficiencies under UV and vis radiation of the ZnO thin films obtained with and without surfactants addition and reference values for methylene blue bleaching in the absence of photocatalyst.

<table>
<thead>
<tr>
<th>Sample/efficiency</th>
<th>Without photocatalyst</th>
<th>Pristine ZnO</th>
<th>SDS 50</th>
<th>SDS 150</th>
<th>DTAB200</th>
<th>DTAB600</th>
<th>DD 500</th>
<th>DD 1000</th>
</tr>
</thead>
<tbody>
<tr>
<td>η_{UV}</td>
<td>12.09</td>
<td>43.90</td>
<td>42.52</td>
<td>45.28</td>
<td>43.68</td>
<td>51.59</td>
<td>44.98</td>
<td>49.43</td>
</tr>
<tr>
<td>η_{vis}</td>
<td>0</td>
<td>12.24</td>
<td>18.28</td>
<td>19.88</td>
<td>14.60</td>
<td>16.27</td>
<td>13.20</td>
<td>15.44</td>
</tr>
<tr>
<td>Δη</td>
<td>100.00</td>
<td>71.59</td>
<td>57.01</td>
<td>56.10</td>
<td>66.58</td>
<td>68.46</td>
<td>70.65</td>
<td>68.76</td>
</tr>
</tbody>
</table>

The relative decrease in efficiency was evaluated using Eq. (5):

\[ Δη = \frac{η_{UV} - η_{vis}}{η_{UV}} \times 100\% \]  

As the data in Table 6 show, the relative decrease in efficiency strongly depends on the surfactant used for obtaining the layer while its concentration has little influence (variations below 3%). The data show that lower loss in the photocatalytic efficiency corresponds to the thin films obtained using ionics surfactants (SDS and DTAB), that also show the best wetting behavior. The DTAB600 thin film has an encouraging photocatalytic efficiency that can be correlated with its low reflectance (R < 8%) and highest roughness. The highest VIS efficiency corresponds to the SDS, 150 and can be correlated with an increased crystallinity and possible Na+ doping that supports the formation of oxygen vacancies and enhances the production of HO· active species, according to the lattice Eq. (6), written by using the Kroeger-Vink notation:

\[ 2Na : ZnO \rightarrow 2Na_{2}O^{+} + O^{2-} + V_{O}^{0} \]  

4. Conclusions

Zinc oxide thin films were obtained through spray pyrolysis deposition, using zinc acetate and acetylacetone in water–ethanol solutions, and three surfactants with linear C12 tail (SDS, DTAB, DD), at concentrations above and below the critical micelle concentration.

The interaction mechanisms of the zinc precursor with the surfactants has as main effect an increase in the local Zn2+ concentration with faster nucleation, at the droplets surface and in the micelles vicinity. Attractive interactions (with SDS) lead to denser structures and smooth films while the weaker interactions (DD, DTAB) lead to more random (amorphous) structures. The films have wetting behavior with large polar components of the surface energy, well supporting the substrate–pollutant interaction in photocatalysis. The photocatalytic experiments proved that the films obtained by surfactant-assisted SPD are active under UV and VIS irradiation, with the largest VIS efficiencies obtained using SDS (20%), when possible Na-doping was outlined.

Acknowledgements

We hereby acknowledge the structural funds project PRO-DD (POS-CCE, O.2.2.1., ID 123, SMIS 2637, No 11/2009) for providing the infrastructure used in this work and the project PNII-UR-TE-2012-3-0177/2013 financed by Romanian National Authority for Scientific Research, CNCS – UEFISCDI.

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Please cite this article in press as: M. Dutta et al., Photocatalytic zinc oxide thin films obtained by surfactant assisted spray pyrolysis deposition, Appl. Surf. Sci. (2014), http://dx.doi.org/10.1016/j.apsusc.2014.02.132