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# ZnO nanowires on glass via chemical routes: A prospective photocatalyst for indoors applications



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ABSTRACT

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## Versatile ZnO nanowires with controlled dimensions and high surface-to-volume ratio were deposited on glass using aqueous solution growth, a simple, environmental-friendly and inexpensive method at 95 °C. The effect of pure ZnO and aluminium doped ZnO (Al<sub>y</sub>Zn<sub>1-y</sub>O, y = 0.01, 0.03, 0.05) seed layers on glass substrates was thoroughly studied against the geometrical features of the as-grown ZnO nanowires. It is revealed that the Al-doped ZnO seed layers possess significantly smaller grain size than the undoped ones (y = 0), while as the Al concentration increases up to y = 0.05 their grain size minimizes down to $19 \pm 1.5$ nm for a thickness of 120 nm. The ZnO nanowires' diameter ranges from 20 to 40 nm following the grain size of the Al<sub>y</sub>Zn<sub>1-y</sub>O seed layer used, while their length is mainly affected from growth time and varies from $175 \pm 25$ nm to $750 \pm 150$ nm. It is demonstrated that ZnO nanowires' arrays grown on glass substrates, pre-coated with Al-doped ZnO seed layers, show superior photocatalytic activity, leading to a prospective photocatalyst, especially for indoors applications.

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## Introduction

Heterogeneous photocatalysis is attracting extensive interest for the degradation of organic pollutants [1–6] and the production of self-cleaning [7,8] and anti-bacterial surfaces [9]. The ability of oxide semiconductor photocatalysts, in particular TiO<sub>2</sub> and ZnO, to degrade a range of organic pollutants such as organic dyes [10,11], pesticides [12] and organic molecules like stearic acid [9,10,13–18] or vapours [19] upon UV or even solar light irradiation, offers many potential applications in areas such as water and air purification, as well as "smart windows" fabrication [1].

Compared to TiO<sub>2</sub>, ZnO is easier to grow either in the form of powder [10] or on top of various substrates [11–16] using chemical techniques, which are environmentally-friendly and quite easy to handle. It has the ability to form versatile nanostructures on different substrate materials, as well as the advantageous characteristic to transform from rods [20,21] to columns and wires [22]. According to various approaches, well oriented ZnO nanowires can be grown on several substrates pre-coated with either a highly crystalline ZnO seed layer annealed at

high temperatures (usually >300 °C) [5,17,18,20,23] or with a non-crystalline ZnO seed layer deposited at temperatures as low as 95 °C [24].

Sakthivel et al. have shown that amongst different semiconducting materials, ZnO is the most active photocatalyst regarding the degradation of acid brown 14 using sunlight as the energy source, since it can absorb more light quanta [25]. Besides, it has been claimed that ZnO is quite an efficient photocatalyst as far as water detoxification is concerned, since it generates  $H_2O_2$  more resourcefully [26] and it has high reaction and mineralization rates [26,27]. However, a serious disadvantage hindering ZnO from broad industrial photocatalytic applications is that it undergoes photocorrosion, especially in humid environments [28,29].

The photocatalytic activity of ZnO thin films can vary considerably and is dependent on many factors, such as film thickness, roughness, grain size and deposition temperature, to name but a few. On the other hand, one-dimensional nanostructured samples offer enhanced photocatalytic activity due to their particularly high surface-to-volume ratio [30,31].

In this work, we investigate the photocatalytic properties of pure and Al-doped ZnO thin films, which were deposited via a sol-gel method, as well as ZnO nanowires' arrays grown on  $Al_yZn_{1-y}O$  (y=0.05) seeded glass substrates from aqueous solutions according to the approach of Andrés Vergés et al. [32] and Vayssieres [33]. It is demonstrated that Al-doped ZnO thin films show better photocatalytic properties than the undoped

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ones, most probably due to their much smaller grain size. The  $Al_yZn_{1-y}O$  (y=0, 0.01, 0.03, 0.05) samples' crystallinity and morphology was thoroughly studied and, by optimizing the growth parameters, ZnO nanowires' arrays with a diameter of  $\sim 30 \pm 10$  nm and a length of  $\sim 150-900$  nm, depending on growth time, were deposited on glass. Evidence is provided that the ZnO nanowires' arrays grown on glass substrates, initially coated with  $Al_yZn_{1-y}O$  (y=0.05) seed layers, present superior photocatalytic properties regarding the degradation of stearic acid under UV-A light illumination (365 nm), which can be mostly attributed to their high surface-to-volume ratio, i.e. aspect ratios L/D (length over diameter) of  $\sim 35$  were achieved.

## **Experimental details**

## Deposition of ZnO:Al seed layers and nanowires

Pure and aluminium doped ZnO thin films ( $Al_vZn_{1-v}O$ , y = 0.01, 0.03, 0.05) with a thickness in the range of 30-330 nm, which were subsequently used as seed layers for the aqueous solution growth (ASG) of ZnO nanowires' arrays, were deposited on glass  $(10 \times 10 \text{ mm}^2 \text{ Corning Eagle 2000 Borosilicate Glass, Specialty})$ Glass Products) substrates using the sol-gel/spin coating technique reported elsewhere [23,24,34–36]. In our experiments, zinc acetate dehydrate [Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O] was first dissolved in a mixture of 2-methoxy ethanol and monoethanolamine at 60 °C. Aluminium nitrate nonahydrate [Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O] served as the dopant source, while the Al molar concentration in the solution was varied from 0 to 5%. The solution concentration was 0.75 mol/L and the molar ratio of monoethanolamine to zinc acetate was kept at 1:1. The resultant solution was stirred for 1 h at 60°C using a magnetic stirrer to yield a homogeneous, clear and transparent solution. The deposition was usually performed within 24 h after the solution was prepared, by spin-coating the substrates, which were rotated at 3000 rpm for 20 s. After processing, the substrates were pre-heated at 350 °C for 10 min to evaporate the solvent and remove the organic residuals from the films. This procedure was repeated up to 6 times (1×, 3×, 6× times). The films were then annealed in air at 600 °C for 60 min. The thickness of the films was measured using a stylus profilometer (Alpha-Step 100, Tencor).

ZnO nanowires' arrays were subsequently grown on Corning glass substrates, pre-coated with  $1 \times -6 \times$  aluminium doped ZnO (Al<sub>y</sub>Zn<sub>1-y</sub>O, y = 0.05) seed layers deposited via the sol-gel technique, using an equimolar (0.01 M) aqueous solution of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and C<sub>6</sub>H<sub>12</sub>N<sub>4</sub> [11,12,24]. Firstly, laboratory Pyrex glass bottles with polypropylene autoclavable screw caps were filled with the solution described above. Subsequently, the substrates pre-coated with the Al<sub>0.05</sub>Zn<sub>0.95</sub>O seed layers were placed in the bottles facing downwards and heated at a constant temperature of 95 °C for 1–10 h in a regular laboratory oven. The samples were then thoroughly washed with MilliQ water (18.2 M $\Omega$  cm) to eliminate residual salts or amino complexes, and dried in air at the same temperature. Prior to deposition, all substrates used were cleaned using a piranha solution (H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub> = 3/1), rinsed with MilliQ water and dried under N<sub>2</sub> gas flow.

#### Characterization techniques

The crystal structure of all samples was determined by X-ray diffraction (XRD) using a Rigaku (RINT 2000) diffractometer with Cu *Ka* X-rays, while their surface morphology was studied by means of a field emission scanning electron microscope (FE-SEM, JEOL JSM-7000F) and an atomic force microscope (AFM) in tapping mode (Digital Instruments – Nanoscope IIIa). The surface roughness (RMS) of the  $Al_yZn_{1-y}O$  seed layers was determined using the scanning probe image processor (SPIP, v. 3.3.5.0) image

processing software for nano- and micro-scale microscopy from image metrology. Finally, UV-vis transmission spectra were recorded using a PerkinElmer (Lambda 950) spectrophotometer over the wavelength range of 250–1100 nm.

#### Photocatalytic activity study

There are many different methods that can be used to determine the activity of photocatalytic surfaces. Popular techniques include those based on the photo-oxidation of organic films such as stearic acid (SA) [13–16,37,38], or organic vapours [19] and contact angle changes [39].

The photocatalytic activity of the ZnO nanostructured samples was determined using SA as a model compound, in which a thin layer of SA was deposited onto the examined sample and its photocatalytic destruction was monitored as a function of time [13–16,37,38]. This method has gained preference over the years since it is simple to set up and run, and needs no dedicated equipment beyond a standard laboratory FTIR spectrometer. Moreover, SA provides a reasonable model compound for solid films that deposit on exterior and interior surfaces, and is very stable under UV illumination in the absence of a photocatalyst film (phenomenon of photolysis). Furthermore, SA can be easily laid down from a methanol or chloroform solution making the test much easier.

In this study, a 0.1 M SA solution in chloroform was spin-coated on the sample surface under investigation at a rotation speed of 500 rpm for 30 s. Samples were then dried at 80 °C in air for 10 min.

The decomposition of SA can be demonstrated by FT-IR spectroscopy through the monitoring of the asymmetric C-H stretching mode of the  $CH_3$  group at  $2958\,cm^{-1}$  and the asymmetric and symmetric C-H stretching modes of the CH<sub>2</sub> group at 2923 and 2853 cm<sup>-1</sup>, respectively. The photocatalytic activity experiments for all ZnO samples regarding the decomposition of SA were performed in ambient air and were repeated for five times demonstrating practically no changes in the %SA conversion, i.e. the observed photocatalytic activity variations were in the order of  $\sim$ 2–3%. The integrated area of the SA C—H stretching peaks (2800-3000 cm<sup>-1</sup>) was monitored using a Fourier transform infrared spectrometer (FT-IR, IRPrestige-21, Shimadzu) before and after black light illumination in a box reactor at certain time intervals. The light source used was an HPK 125W Philips mercury lamp with main emission wavelength at 365 nm and an incident light intensity of 10 mW/cm<sup>2</sup>. For ease in comparison of the photocatalytic activity between different samples, the integrated area of the C—H stretching peaks  $(2800-3000 \text{ cm}^{-1})$ measured at each irradiation time interval was normalized to the initial integrated area (prior to the irradiation) in order to calculate the percentage of SA remaining as a function of irradiation time. Blank experiments (photolysis) were also performed using bare glass substrates under exactly the same conditions applied for the ZnO samples. Finally, the SA disappearance rate (mol/min) and the formal quantum efficiency (FQE) for all ZnO samples were calculated according to the methodology of Mills and Wang [37].

#### **Results and discussion**

Fig. 1 depicts typical X-ray diffraction patterns of the  $Al_{0.03}Zn_{0.97}O$  seed layers deposited by the sol-gel/spin-coating technique after 1, 3 and 6 spinning cycles. The thickness of the 1×, 3× and 6×  $Al_yZn_{1-y}O$  (y=0.01, 0.03, 0.05) seed layers is ~40–55 nm, ~110–120 nm and ~300–330 nm, respectively, depending on the %molar doping of Al. On the other hand, the corresponding thickness for the 1×, 3× and 6× pure ZnO seeds is ~30, ~60 and ~140 nm, respectively. All the diffraction peaks observed for the  $Al_{0.03}Zn_{0.97}O$  seed layers are in good agreement with the JCPDS card (no. 36-1451) for a typical hexagonal wurtzite



**Fig. 1.** XRD patterns of: (a)  $1 \times (\sim 50 \text{ nm thick})$ ; (b)  $3 \times (\sim 110 \text{ nm thick})$  and (c)  $6 \times (\sim 300 \text{ nm thick})$  aluminium doped ZnO seed layers deposited by the sol-gel/spin-coating technique, with 3% molar concentration of Al.

type crystal and show a clear preferential (002) orientation along the *c*-axis, i.e. perpendicular to the substrate applied (see Fig. 1(a)–(c)). It can be also seen that no other characteristic peaks corresponding to possible impurities, such as zinc nitrate or zinc hydroxide, are observed in the XRD patterns.

In particular, the red solid line in Fig. 1(a) depicts the X-ray diffraction pattern of a 50 nm-thick  $(1 \times)$  Al<sub>0.03</sub>Zn<sub>0.97</sub>O seed layer, which was deposited by sol-gel on a Corning glass substrate at 600 °C. A single diffraction peak centred at 34.40° can be only observed indicating a clear preferential growth orientation along the (002) crystallographic direction. Similarly, Fig. 1(b) and (c) display the X-ray diffraction patterns of 110 nm-  $(3 \times)$  and  $300 \text{ nm-thick} (6 \times) \text{Al}_{0.03} \text{Zn}_{0.97} \text{O}$  seed layers deposited on Corning glass substrates under the same experimental conditions (green and blue solid lines in Fig. 1(b) and (c), respectively). Once more, it can be readily seen that only the (002) diffraction peak occurs, demonstrating a preferential growth along the *c*-axis. Moreover, it can be observed from Fig. 1(a–c) that both  $3 \times$  and  $6 \times Al_{0.03}Zn_{0.97}O$ seed layers show narrower (002) reflections with significantly higher intensity than the corresponding  $1 \times Al_{0.03}Zn_{0.97}O$  sample, indicating in general an enhanced crystallinity of the  $Al_{v}Zn_{1-v}O$ (y = 0.01, 0.03, 0.05) samples with increasing thickness.

The mean crystallite dimensions (d) of the  $Al_yZn_{1-y}O(y=0.01, 0.03, 0.05)$  samples were calculated using Scherrer's equation:

$$d = \frac{K\lambda}{(\beta^2 - \beta_0^2)^{1/2} \cos\theta} \tag{1}$$

where  $\beta$  is the measured broadening of a diffraction line peak at an angle of  $2\theta$  at half its maximum intensity (FWHM) in radians,  $\beta_0$  is the instrumental broadening,  $K = 180/\pi$ ,  $\lambda$  is the X-rays wavelength (0.154056 nm) and  $\theta$  is the Bragg diffraction angle. By fitting the (0 0 2) diffraction peak to Scherrer's equation, crystallite size values between 26.52 and 13.23 nm were obtained.

Fig. 2 presents the crystallite size as calculated using Scherrer's equation for  $2\theta$  = 34.40° (black curves with squares), along with the

thickness of the  $Al_{\nu}Zn_{1-\nu}O$  films (blue curves with stars), as a function of the number of the layers and %Al concentration. It was first observed that the crystallite size increases with the number of the spin-coated layers for pure ZnO films (y=0), i.e. it displays a value of 28.44 nm for  $1 \times$  ZnO while it reaches 32.15 and 38.19 nm for  $3 \times$  and  $6 \times$  ZnO, respectively, indicating better crystallinity of the pure ZnO seed layers with increasing thickness, as it has been also previously reported [18,23,35]. However, the same behaviour is not observed for the Al-doped ZnO seed layers (y = 0.01, 0.03, 0.05), since, for all %Al concentrations, the crystallite size slightly drops with increasing thickness. For example, in the case of Al<sub>0.05</sub>Zn<sub>0.95</sub>O seed layers, the crystallite size varies from 15.85 nm for 1×  $Al_{0.05}Zn_{0.95}O$  to 13.54 and 13.23 nm for 3× and 6×  $Al_{0.05}Zn_{0.95}O$ , respectively. It is obvious from Fig. 2 that Al doping leads to much smaller crystallite size compared to pure ZnO, something that will strongly affect the photocatalytic activity of the  $Al_v Zn_{1-v}O$  (*y* = 0.01, 0.03, 0.05) samples (vide infra).

Furthermore, it can be also noticed from Fig. 2 that for a constant number of layers, an increase in Al concentration hardly affects the thickness of the as-grown  $Al_yZn_{1-y}O$  thin films. At the same time the crystallite size reduces gradually with increasing Al doping. This phenomenon is attributed to the nucleation mechanism of the ZnO phase, since, generally, an increase of Al concentration will enhance the nucleation of the ZnO phase and consequently result in smaller crystallite size [35]. The reason is that the repeated spin-coating procedures allow the Al atoms to relocate at positions with lower free energy and to grow laterally [35]. Consequently, the Al-doped ZnO films become denser.

Fig. 3 exhibits the variation of grain size and surface roughness (RMS) of the as-grown  $Al_yZn_{1-y}O(y=0,0.01,0.03,0.05)$  seed layers as a function of %Al concentration and number of spin-coated layers. One can notice that for pure ZnO seed layers (y=0), the grain size (black squares in Fig. 3) as well as the roughness (blue stars in Fig. 3) gradually increases with thickness, i.e. the number of the spin-coated layers; both the grain size and the roughness of the Al-doped ZnO samples are hardly affected by the thickness. Moreover, increasing the %Al doping concentration from 1 to 5% does not seem to influence considerably the grain size of the  $3 \times Al_yZn_{1-y}O$  samples the grain size varies from 22 nm (y=0.01) to 19 nm (y=0.05). However, all the  $Al_yZn_{1-y}O$  (y=0.01, 0.03, 0.05) samples show much smaller grain size values than the pure ZnO



**Fig. 2.** Crystallite size as calculated using Scherrer's equation for  $2\theta = 34.40^{\circ}$  (black curves with squares), along with the thickness of the Al<sub>y</sub>Zn<sub>1-y</sub>O (y = 0, 0.01, 0.03, 0.05) seed layers (blue curves with stars), as a function of the number of the layers of the samples and the %Al molar concentration.



**Fig. 3.** Grain size (black squares) and roughness (blue stars) vs. thickness of the sol-gel deposited  $Al_yZn_{1-y}O(y=0, 0.01, 0.03, 0.05)$  seed layers as a function of the % Al molar concentration.

seed layers (*y*=0). In particular, 5% Al-doped ZnO samples have a grain size of ~27 ± 2 nm for a thickness of around 55 nm (1×), ~19 ± 1.5 nm for a thickness of ~120 nm (3×), and ~18 ± 3 nm for a thickness of ~330 nm (6×), respectively. On the other hand, pure ZnO seed layers show grain size values of  $35 \pm 2$ ,  $67 \pm 4$  and  $92 \pm 5$  for 1×, 3× and 6× spinning cycles, respectively [18,23].

Fig. 4(a)–(c) presents AFM images (scan size  $1 \times 1 \mu$ m) of the 55 nm- (1×), 120 nm- (3×) and 330 nm-thick (6×) Al<sub>0.05</sub>Zn<sub>0.95</sub>O seed layers deposited on Corning glass substrates via sol–gel at 600 °C, while Fig. 4(d) illustrates the AFM image of the pure 6× ZnO sample (140 nm-thick). The corresponding SEM micrographs of the 5% Al-doped ZnO seed layers [55 nm- (1×), 120 nm- (3×) and 330 nm- (6×)], along with the pure 6× ZnO sample are presented in Fig. 4(e)–(h), respectively. It can be observed that all the Al<sub>0.05</sub>Zn<sub>0.95</sub>O seed layers are homogeneous, crack-free and densely packed, while their grains are significantly smaller than those of the 6× pure ZnO film (y=0). As it is shown in Fig. 4(a)–(d) and Fig. 4 (e)–(h), there is a good agreement between the results revealed from AFM and SEM analyses regarding the grain size and the surface morphology of the Al<sub>y</sub>Zn<sub>1-y</sub>O (y=0, 0.05) seed layers.

All the Al<sub>v</sub>Zn<sub>1-v</sub>O (y = 0, 0.01, 0.03, 0.05) seed layers are highly transparent in the visible regime and exhibit a sharp absorption band in the UV region (see Fig. 5). The presence of a transmittance peak at  $\sim$ 345 nm can be attributed to excitonic resonances [40]. As it is clearly seen in the inset of Fig. 5, the UV absorption edge of the  $Al_{v}Zn_{1-v}O$  (y = 0, 0.01, 0.03, 0.05) seed layers is blue-shifted with increasing %Al doping concentration, indicating a broadening of the optical band gap [41,42]. The optical energy gap values  $(E_{gap})$  of the  $Al_v Zn_{1-v}O(y=0, 0.01, 0.03, 0.05)$  seed layers were determined by the extrapolation of the linear portion of  $(\alpha hv)^2$  vs. hv plots ("Tauc" plots) and are presented in Table 1. It should be noted that the adjusted R-square statistic varies from 0.99879 to 0.99972 indicating that the model used for the determination of  $E_{gap}$  is adequate. Table 1 clearly illustrates that as the %Al concentration rises from 0 to 5%, the optical band gap increases, as expected from the blue shift of the UV absorption edge reported above. Specifically, for the  $3 \times Al_y Zn_{1-y}O$  seed layers, the  $E_{gap}$  takes values of 3.276, 3.281, 3.292 and 3.314 eV for *y* = 0, 0.01, 0.03 and 0.05, respectively. This change in optical band gap can be explained in terms of the Burstein-Moss band gap widening due to the electron-electron and electron-impurity scattering [43,44].



**Fig. 4.** (a-c) AFM images (scan size  $1 \times 1 \mu m$ ) of the  $1 \times (\sim 55 \text{ nm thick})$ ,  $3 \times (\sim 120 \text{ nm thick})$  and  $6 \times (\sim 330 \text{ nm thick})$  Al<sub>y</sub>Zn<sub>1-y</sub>O seed layers on Corning substrates with an Al molar concentration of 5%, (d) AFM image of the pure  $6 \times \text{ ZnO}$  seed layer ( $\sim 140 \text{ nm thick}$ ), while (a-h) illustrate the corresponding SEM images.



**Fig. 5.** Optical transmittance spectra of  $3 \times Al_y Zn_{1-y}O$  (y = 0, 0.01, 0.03, 0.05) seed layers deposited by the sol-gel/spin-coating technique. In the inset of Fig. 5 one can notice the blue shift of the transmission spectrum with increasing %Al molar concentration.



Optical energy band gap ( $E_{gap}$ , eV) of the Al<sub>y</sub>Zn<sub>1-y</sub>O seed layers, as determined using "Tauc" plots of  $\alpha^2$  as a function of  $h\nu$ .

No. of layers	Al concentration					
	0% (eV)	1% (eV)	3% (eV)	5% (eV)		
$1 \times 3 \times 6 \times$	3.272 3.276 3.288	3.278 3.281 3.291	3.284 3.292 3.297	3.287 3.314 3.317		

Fig. 6(a)–(f) illustrates SEM images of the ZnO samples deposited by ASG for 2–10 h on Corning glass substrates pre-coated with 3× (~120 nm thick) Al<sub>0.05</sub>Zn<sub>0.95</sub>O seed layers. As it can be observed, in all cases, the substrates were covered with quite dense and uniform ZnO nanowire arrays. The nanowires emerge perpendicular to the substrate applied, with almost no nanowires tilted from the surface (except of cases in Fig. 6(e) and (f)), while they all display a hexagonal cross-section. It is furthermore observed that the nanowires' diameter remains constant in the range of  $30 \pm 10$  nm despite the growth time, indicating that the control of the diameter is directly related with the grain size of the Aldoped ZnO seed layer [23,24]. The length of the ZnO nanowires grown on  $3 \times Al_{0.05}Zn_{0.95}O$  seed layer is 150-200 nm for 2 h, 600-700 nm for 5 h, and 600-900 nm for 10 h growth, respectively. Taking into consideration the nanowires' dimensions

mentioned above, i.e. their diameter and length, one can estimate



**Fig. 6.** SEM images of the ZnO samples deposited by aqueous solution growth for 2 h (a, b), 5 h (c, d) and 10 h (e, f) on Corning glass substrates pre-coated with  $3 \times (\sim 120 \text{ nm thick}) \text{ Al}_{0.05}\text{Zn}_{0.95}\text{O}$  seed layers.



**Fig. 7.** Normalized integrated area vs. irradiation time for 3× pure ZnO and 3× Al<sub>0.05</sub>Zn<sub>0.95</sub>O seed layers as well as ZnO nanowires grown for 2–10 h on Corning glass substrates pre-coated with 3× Al<sub>0.05</sub>Zn<sub>0.95</sub>O seed layers, respectively. For comparison reasons, the photolysis curve (black solid squares) is also presented.

#### Table 2

Initial stearic acid disappearance rate (mol/min) and formal quantum efficiency (FQE, see Mills et al. [37]) at 15 min, for the Al<sub>y</sub>Zn<sub>1-y</sub>O (y = 0, 0.05) seed layers as well as the chemically grown ZnO nanowires' arrays.

	Photolysis	3× ZnO	3× Al-ZnO (5%)	2 h ASG on 3× Al–ZnO	5 h ASG on 3× Al–ZnO	10 h ASG on $3 \times$ Al–ZnO
Initial SA disappearance rate (mol/min) Formal quantum efficiency, (FQE) <sub>(SA)</sub> /10 <sup>-3</sup>	$\begin{array}{c} 3.05 \times 10^{-10} \\ 0.03 \end{array}$	$\begin{array}{c} 1.65 \times 10^{-8} \\ 1.75 \end{array}$	$\begin{array}{c} 3.88\times10^{-8}\\ 4.10\end{array}$	$\begin{array}{c} 5.18 \times 10^{-8} \\ 5.49 \end{array}$	$\begin{array}{c} 5.98 \times 10^{-8} \\ 6.33 \end{array}$	$\begin{array}{c} 4.48 \times 10^{-8} \\ 4.75 \end{array}$

the aspect ratio (length over diameter, L/D) of the ZnO nanowires grown on Corning glass substrates pre-coated with  $3 \times$  (~120 nm thick) Al<sub>0.05</sub>Zn<sub>0.95</sub>O seed layers. L/D is ~10 for ZnO nanowires grown by ASG for 2 h, while L/D becomes ~35 and ~45 for 5 and 10 h growth, respectively.

If one looks carefully at the SEM images of the as-grown ZnO nanowires, it could be noticed that the sample with the best orientation along the *c*-axis is that grown on the  $\sim$ 120 nm-thick (3×) Al<sub>0.05</sub>Zn<sub>0.95</sub>O seed layer (see Fig. 6), which at the same time shows a considerable aspect ratio *L/D* value of  $\sim$ 35 (see Fig. 6(c) and (d)).

Fig. 7 presents the normalized integrated area vs. irradiation time curves for ZnO nanowires fabricated by ASG on  $3 \times (\sim 120 \text{ nm} \text{ thick}) \text{Al}_{0.05}\text{Zn}_{0.95}\text{O}$  for 2–10 h at 95 °C. For comparison reasons, the corresponding curves for undoped  $3 \times \text{ZnO}$  and  $3 \times \text{Al}_{0.05}\text{Zn}_{0.95}\text{O}$  seed layers along with the photolysis curve (no catalyst present) are also displayed in Fig. 7. It can be noticed that the stand-alone  $3 \times \text{Al}_y\text{Zn}_{1-y}O(y = 0.05)$  seed layer, as well as all the ZnO nanowires' arrays grown for 2–10 h exhibit more than 80% SA conversion at 15 min upon UV-A irradiation. At the same time, the pure  $3 \times \text{ZnO}$  seed layer shows substantially less %SA conversion, i.e. ~53% at 15 min.

The photocatalytic activity of the Al<sub>y</sub>Zn<sub>1-y</sub>O (y = 0, 0.05) seed layers as well as the ZnO nanowires' arrays is summarized in Table 2, where the SA disappearance rate (mol/min) and the formal quantum efficiency (FQE) are displayed, following the methodology explained by Mills and Wang [37]. It can be readily observed that the  $3 \times Al_{0.05}Zn_{0.95}O$  seed layer shows significantly better activity (FQE =  $4.10 \times 10^{-3}$  at 15 min) than the pure  $3 \times ZnO$  one (FQE =  $1.75 \times 10^{-3}$  at 15 min), since as already mentioned, it has much smaller grain size, i.e.  $\sim 19 \pm 1.5$  nm compared to  $\sim 67 \pm 4$  nm for pure  $3 \times ZnO$  (see Fig. 3), and thus displays higher effective surface area.

ZnO nanowires grown via ASG at 95 °C for 5 h on a Corning glass substrate, which was pre-coated with a  $3 \times Al_{0.05}Zn_{0.95}O$  seed layer, show by far the best photocatalytic activity (FQE =  $6.33 \times 10^{-3}$  at 15 min), degrading SA by ~94.46% at 15 min and ~99% at 30 min,

respectively. This behaviour is probably attributed to the enhanced growth orientation along the *c*-axis of the aqueous solution grown ZnO nanowires (see Fig. 6(c) and (d)), together with their high aspect ratio (L/D ~35). As presented in Table 2, as the growth time increases to 10 h and ZnO wires become higher (and reclined, as seen in Fig. 6(e) and (f)) with L/D ~45, the photocatalytic activity of the samples is getting smaller giving a FQE value of  $4.75 \times 10^{-3}$  (86.18% SA conversion at 15 min). It can be thus finally noticed that one of the most critical parameters which strongly influences the photocatalytic activity of Al<sub>y</sub>Zn<sub>1-y</sub>O (*y* = 0, 0.01, 0.03, 0.05) seed layers is grain size. In the case of the ZnO nanowires arrays, it is mostly enhanced *c*-axis preferred growth orientation and large aspect ratio (L/D) values, which lead to high FQEs.

## Conclusions

ZnO nanowires, highly oriented along the *c*-axis, were grown at 95°C for 2-10h from an aqueous solution on Corning glass substrates, which were pre-coated with Al-doped ZnO seed layers deposited via a sol-gel technique. It is observed that the Al-doped ZnO seed layers ( $Al_vZn_{1-v}O$ , y=0.01, 0.03, 0.05) possess significantly smaller grain size than the undoped ones (y=0). The ZnO nanowires' diameter can be accurately tuned by varying the grain size of the seed layer used, while their length is mainly affected from growth time. All  $Al_{v}Zn_{1-v}O(y = 0, 0.01, 0.03, 0.05)$  samples show remarkable photocatalytic activity regarding the %conversion of stearic acid. The  $3\times~Al_{0.05}Zn_{0.95}O$  seed layer shows significantly better activity (FQE =  $4.10 \times 10^{-3}$  at 15 min) than the pure  $3 \times ZnO$  one (FQE =  $1.75 \times 10^{-3}$  at 15 min), due to its much smaller grain size. ZnO nanowires' arrays demonstrate, however, superior photocatalytic activity compared with the stand-alone seed layers, most probably because of their large surface-tovolume ratio. In particular, ZnO nanowires grown for 5 h on a  $3\times$  $({\sim}120\,nm$  thick)  $Al_{0.05}Zn_{0.95}O$  seed layer exhibit the best photocatalytic activity (FQE =  $6.33 \times 10^{-3}$  at 15 min), a behaviour which is attributed to their better c-axis alignment along with higher wires' aspect ratio (L/D  $\sim$ 35), i.e. larger surface-to-volume ratio.

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