

Light-induced self-cleaning properties of ZnO nanowires grown at low temperatures

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ABSTRACT

Highly *c*-axis oriented ZnO nanowires' arrays were grown on glass substrates using an aqueous solution approach, in which the growth temperature does not exceed 95 °C in any step of the synthesis. Both their photocatalytic and wetting properties were studied upon ultraviolet (UV) light irradiation. It is revealed that ZnO nanowires' arrays show advanced photocatalytic activity, along with a remarkable reversible photo-induced transition from hydrophobic to super-hydrophilic under UV light exposure, reaching a nearly zero contact angle in short time. The capability to control the morphological characteristics of ZnO nanowires via the deposition of an amorphous seed layer is discussed, which can be significant for self-cleaning applications.

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1. Introduction

The self-cleaning mechanism is a unique dual-action property of surfaces. The photocatalytic action, in which the coating reacts with daylight to break down organic dirt, and the hydrophilic action, in which the rainwater spreads uniformly across the surface, takes away the loosened dirt and dries quickly without leaving any streaks. Hence, the synergetic effect of these two actions is quite important in sustaining the self-cleaning effect [1]. Control of the self-cleaning property has attracted great interest because of its importance in fundamental research and industrial fields. Most of these applications involve solid surfaces such as glasses and flexible membranes or even waterproofing textiles [2,3].

Among other materials, the wetting properties of metal oxides, mainly of TiO₂ and ZnO, have been widely studied, since irradiation with UV light may significantly modify their wettability [4–7]. Recent studies revealed that micro- and nano-structures exhibiting hierarchical roughness can be super-hydrophobic [8,9] and reversibly switched to super-hydrophilic [10], opening the way for

the construction of the future-generation of smart, self-cleaning surfaces [11].

Furthermore, ZnO and TiO₂ have been widely used as photocatalysts because of their ability to degrade organic dyes [12,13], pesticides [14], human metabolite and priority pollutants listed by U.S. EPA, such as trichloroethylene (TCE), 2,4-dichlorophenol (DCP) etc. [15–18] and organic molecules such as stearic acid (SA) [9,12,19–24] or vapours [25] upon UV irradiation.

Comparing the above metal oxides, one can easily distinguish ZnO for its ability to form nanostructures as well as its advantageous characteristic to transform from rods [10,26] to columns and wires [27]. Besides, it has been reported that ZnO shows better activity than TiO₂ in the photodegradation of some dyes in aqueous solutions since it can absorb more light quanta [28].

According to various approaches [5,10,23,24,29,30], well-oriented ZnO nanowires can be grown on several substrates pre-coated with a highly crystalline ZnO seed layer annealed at high temperatures (usually >300 °C).

In the present work, we investigate the self-cleaning properties of *c*-axis oriented ZnO nanowires grown at 95 °C. More specifically, the photo-induced reversible wetting properties of the as-grown samples, along with the degradation of SA, under UV-A light illumination (365 nm) were studied, in relation to deposition time and their resultant morphological characteristics. The ZnO nanowires'

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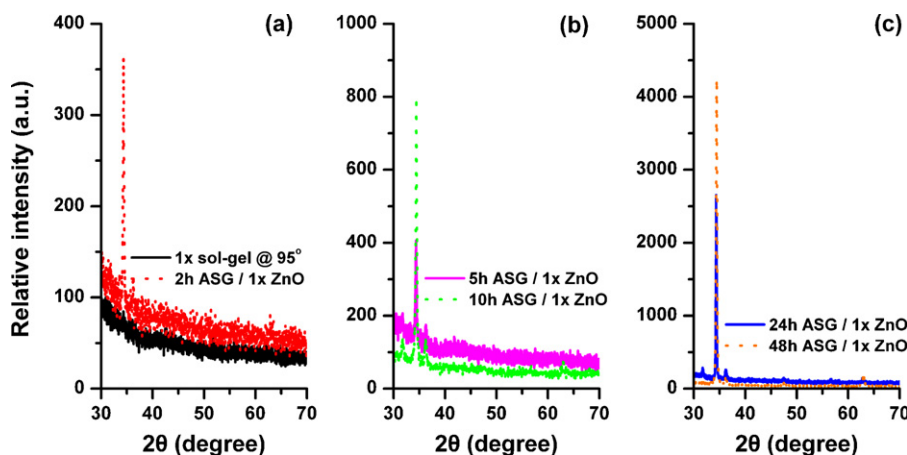


Fig. 1. XRD patterns of (a) ZnO nanowires grown by ASG for 2 h (red dotted curve) on Corning glass substrates pre-coated with 1× ZnO seed layer (black solid curve), (b) ZnO nanowires grown by ASG on 1× ZnO for 5 h (magenta solid curve) and 10 h (green dotted curve), (c) ZnO nanowires grown by ASG on 1× ZnO for 24 h (blue solid curve) and 48 h (orange dotted curve). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

arrays were grown on ZnO pre-coated glass substrates via aqueous solution growth (ASG), firstly reported by Andrés Vergés et al. [31] and Vayssieres [32]. We demonstrate that a non-crystalline ZnO seed layer deposited at temperatures as low as 95 °C can promote the growth of transparent *c*-axis oriented ZnO nanostructured samples with enhanced photocatalytic activity and reversible hydrophilicity.

2. Experimental details

2.1. Deposition of ZnO seed layers and nanowires

ZnO nanowires' arrays were synthesized from zinc nitrate in an aqueous solution under hydrothermal conditions [29,31–33]. The procedure consisted of two steps: In the first step, ZnO seed layers were prepared by a sol-gel/spin coating technique on glass substrates (Corning Eagle 2000 Borosilicate Glass, Specialty Glass Products) [23,24,29]. In detail, Zinc acetate dehydrate [$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$] was first dissolved in a mixture of 2-methoxy ethanol and monoethanolamine at room temperature (RT). The concentration of zinc acetate 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 to yield a homogeneous, clear, and transparent solution using a magnetic stirrer. Consequently, 30 μL of the precursor solution were dropped onto Corning glass substrates, which were then spun at 2000 rpm for 20 s. After processing, the substrates were heated at 95 °C for 24 h in a regular laboratory oven (Mettmert UNP 500) to evaporate the solvent in the films. This procedure was repeated one (1×) and three (3×) times.

In the second step, ZnO nanowires' arrays were subsequently grown on Corning glass substrates, pre-coated with 1× and 3× ZnO seed layers, using an equimolar (0.01 M) aqueous solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{C}_6\text{H}_{12}\text{N}_4$ [13,14,31]. Initially, laboratory Pyrex glass bottles with polypropylene autoclavable screw caps were filled with the 0.01 M aqueous solution. Then, the substrates with the pre-coated ZnO seed layers were placed in the bottles facing downwards and heated at a constant temperature of 95 °C for 2–48 h in a regular laboratory oven (Mettmert UNP 500). Finally, the samples were dipped into MilliQ (18.2 M $\Omega \text{ cm}$) water 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 ($\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2 = 3/1$), rinsed with MilliQ water and dried under N_2 gas flow.

2.2. Characterization techniques

The crystal structure of the ZnO samples was determined by X-ray diffraction (XRD) using a Rigaku (RINT 2000) diffractometer with Cu K α ($\lambda = 1.5406 \text{ \AA}$) X-rays for $2\theta = 30.0\text{--}70.0^\circ$, while their surface morphology was studied by means of a field emission scanning electron microscope (FE-SEM, JEOL JSM-7000F). Raman measurements were performed with a Nicolet Almega XR micro-Raman system within 100 and 1000 cm^{-1} using a 473 nm laser. Finally, UV–vis transmission spectra were recorded using a Shimadzu UV-2401 spectrophotometer over the wavelength range of 190–990 nm.

2.3. Photocatalytic activity study

The photocatalytic activity of our ZnO samples was determined using stearic acid as a model compound, in which a thin layer of SA is deposited onto their surface and their photocatalytic degradation is monitored as a function of time [12,19–24]. This method has gained preference over the years since SA provides a reasonable model compound for solid films that deposit on exterior and interior surfaces. It is very stable under UV illumination in the absence of a photocatalytic film (phenomenon of photolysis). Finally, it can be easily laid down from a methanol or chloroform solution making the test much easier.

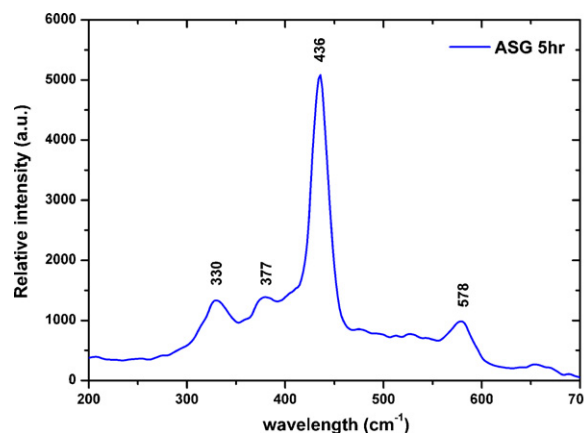


Fig. 2. Raman spectra of ZnO nanowires deposited on Corning glass substrates pre-coated with 1× ZnO seed layer for 5 h.

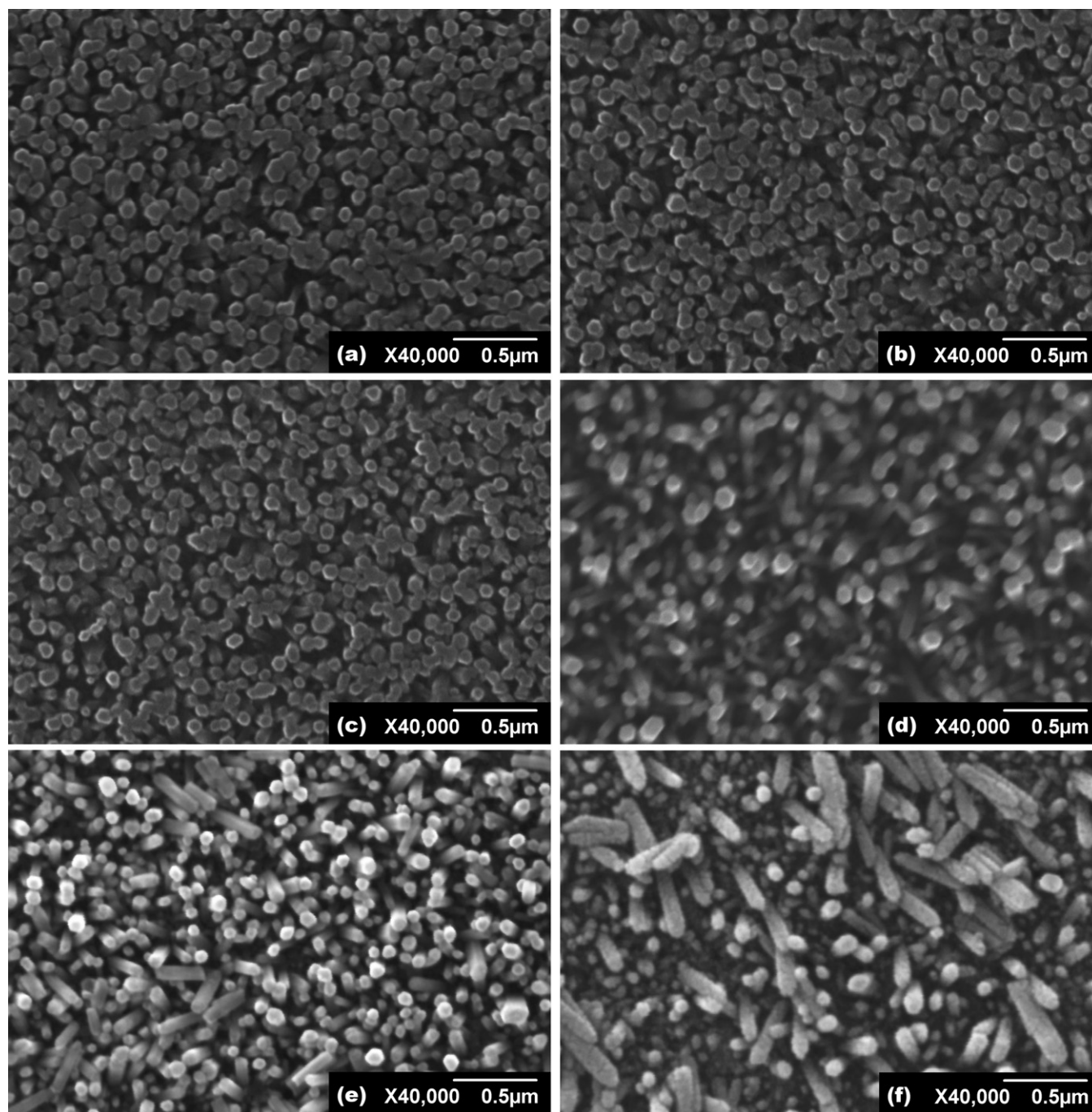


Fig. 3. SEM images of ZnO nanowires grown by ASG on Corning glass substrates pre-coated with (a)–(e) $1 \times$ ZnO for 2 h, 5 h, 10 hr, 24 h, and 48 h and (f) ZnO nanowires deposited by aqueous solution growth for 48 h on Corning glass substrates pre-coated $3 \times$ ZnO seed layer, respectively.

In order to deposit SA on the ZnO seed layers and nanostructures, a droplet of $30 \mu\text{L}$ of a 0.1 M SA solution in chloroform was spin-coated on the sample surface 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 was demonstrated by Fourier transform infrared spectroscopy (FT-IR, IRPrestige-21, Shimadzu) 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_2 group at 2923 and 2853 cm^{-1} , respectively. The photocatalytic activity experiments on all ZnO samples were performed at ambient temperature. The integrated area of the stearic acid C–H stretching peaks ($2800\text{--}3000 \text{ cm}^{-1}$) was

monitored before and after black light illumination in a box reactor at certain time intervals. The light source used was a HPK 125 W Philips mercury lamp with main emission wavelength at 365 nm and an incident light intensity of 8.9 mW/cm^2 . For ease in comparison of the photocatalytic activity between different samples, the integrated area of the C–H stretching peaks ($2800\text{--}3000 \text{ cm}^{-1}$) measured at each irradiation time interval was normalized to the initial integrated area (prior to the irradiation) in order to calculate the percentage of stearic acid remaining as a function of irradiation time.

Blank experiments (photolysis) were also performed using bare Corning Eagle 2000 Borosilicate substrates (glass free of ZnO) under exactly the same conditions as used for the ZnO samples.

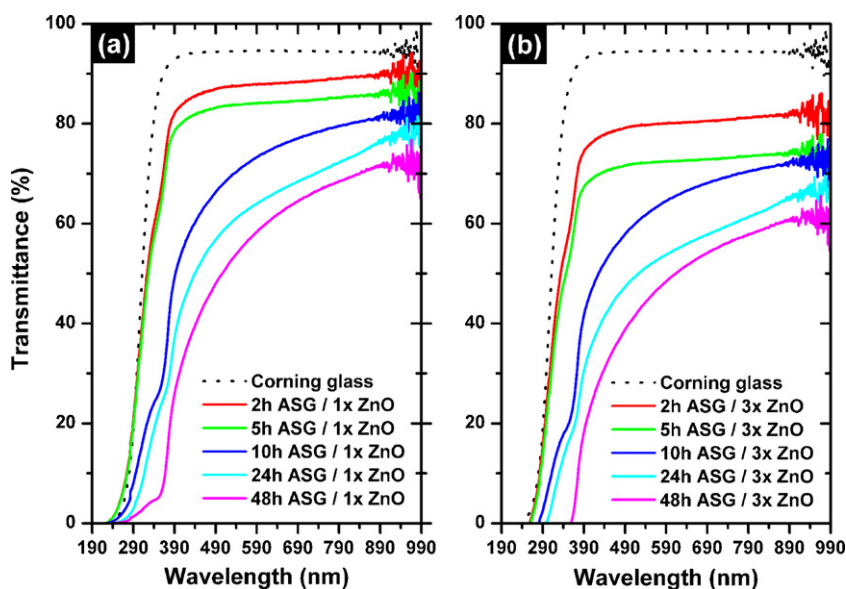


Fig. 4. Optical transmittance spectra of ZnO nanowires grown by ASG for 2–48 h on Corning glass substrates pre-coated with 1 × (a) and 3 × (b) ZnO seed layers, respectively.

2.4. Wettability study

The surface wettability of the ZnO nanowires was evaluated by water contact angle measurements performed by the sessile drop method. A 10 μ L MilliQ water droplet was gently positioned on the surface of the samples using a microsyringe. A CCD camera-lens optical system was used to capture digital images of the droplet profile from a location parallel to the substrate. Contact angles were subsequently determined from the corresponding pictures using an image-processing algorithm, and a mean value was calculated from at least five individual measurements. Light induced hydrophilicity was evaluated in atmospheric air and a temperature of 25 °C by irradiating the samples at certain time intervals using a Hamamatsu Hg lamp, centered at 365 nm, with an intensity of 4 mW/cm² at the position of the samples. After each irradiation period, a 10 μ L water drop was placed on the irradiated area and the corresponding contact angle was measured again. Following irradiation, the samples were stored in the dark at RT and then the measurements were conducted again.

3. Results and discussion

3.1. Characterization of ZnO nanowires

Fig. 1 depicts typical X-ray diffraction patterns of 1 × ZnO seed layer deposited on Corning glass substrates by the sol-gel/spin-coating technique at 95 °C (see black line of Fig. 1a) and ZnO nanowires' arrays grown via ASG on top for 2–48 h (Fig. 1a–c). There is no evidence of diffraction peaks for the 1 × ZnO seed layer (same behavior is valid for 3 ×), indicating that the samples are largely amorphous. On the other hand, ZnO samples prepared via ASG for 2–48 h on pre-coated Corning glass substrates show a clear preferential growth orientation along the (002) crystallographic direction, i.e. perpendicular to the Corning glass substrates. Therefore, it can be concluded that the amorphous ZnO seed layers indeed assist the preferential growth of the chemically grown ZnO samples along the c-axis, i.e. the (002) crystallographic direction.

The reason for superior alignment on ZnO seeded substrates is due to the polar nature of the ZnO surface and the matching lattice structure [24,34]. Moreover, it can be observed that as the growth time of ASG increases from 2 to 48 h, the ZnO samples show narrower (002) reflections with significantly higher intensity

(Fig. 1a–c). For example, the Full Width at Half Maximum (FWHM) value for the (002) peak is 0.286° and 0.179° in the case of the ZnO nanowires' arrays grown on 1 × ZnO seeded substrates for 2 and 48 h, respectively.

All the diffraction peaks observed are in good agreement with the JCPDS card (No. 36-1451) for a typical hexagonal wurtzite type ZnO crystal. 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.

The Raman spectrum of ZnO nanowires' arrays grown on 1 × ZnO seeded substrates at 95 °C for 5 h is shown in Fig. 2 and is characteristic for all deposition times (note that the Raman spectra of the ZnO samples grown on 3 × ZnO seeded substrates are also similar to the one presented in Fig. 2). The observed phonon frequencies in these Raman spectra are: 330 cm⁻¹ (multiple-phonon scattering processes), 377 cm⁻¹ (A₁(TO)), 436 cm⁻¹ (E₂(high)) and 578 cm⁻¹ (E₁(LO)), which are in good agreement with those reported in the literature [35–37]. The E₂ (high) mode at 436 cm⁻¹, having the strongest intensity for all grown samples, is characteristic of the ZnO hexagonal wurtzite structure [37]. Therefore, the recorded

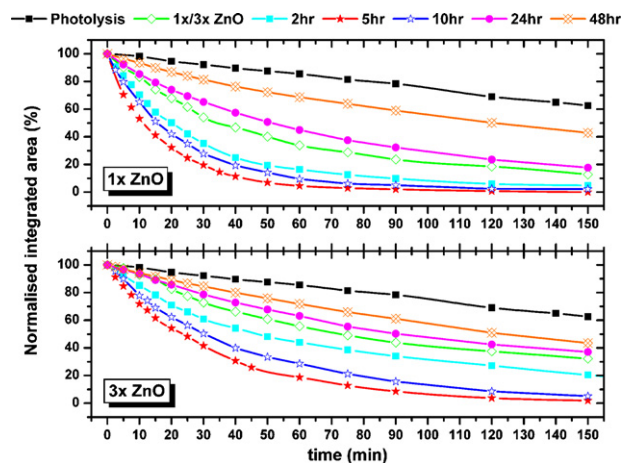


Fig. 5. Normalized integrated area vs. irradiation time for ZnO nanowires grown by aqueous solution growth for 2–48 h on Corning glass substrates pre-coated with 1 × (top) and (bottom) 3 × ZnO seed layer, respectively. For comparison reasons, the photolysis curve (black solid squares) is also presented.

Table 1

Photocatalytic activity at 30 min, initial stearic acid disappearance rate (mol/min) and formal quantum efficiency (FQE, see Mills et al. [40]) for the ZnO samples deposited via ASG. Fields marked with superscript 'a' correspond to data for ZnO nanowires grown on 1× ZnO seed layer, while fields marked with superscript 'b' correspond to data for ZnO nanowires grown on 3× ZnO seed layer, respectively.

	α (%) at 30 min	Initial SA disappearance rate (mol/min)	Formal quantum efficiency, (FQE) _(SA) /10 ^{−3}
Photolysis	7.85	4.44×10^{-10}	0.047
1× seed layer	46.00	1.05×10^{-8}	1.117
3× seed layer	27.19	5.32×10^{-10}	0.0563
2 h ASG on			
1×	64.79 ^a	3.99×10^{-8a}	4.238 ^a
3×	39.22 ^b	8.17×10^{-9b}	0.866 ^b
5 h ASG on			
1×	80.44 ^a	5.58×10^{-8a}	5.908 ^a
3×	58.44 ^b	3.06×10^{-8b}	3.246 ^b
10 h ASG			
1×	72.26 ^a	3.70×10^{-8a}	3.922 ^a
3×	49.65	1.93×10^{-8b}	2.043 ^b
24 h ASG			
1×	34.79 ^a	1.12×10^{-8a}	1.186 ^a
3×	21.40 ^b	2.06×10^{-9b}	0.219 ^b
48 h ASG			
1×	18.72 ^a	4.52×10^{-9a}	0.478 ^a
3×	15.50 ^b	3.62×10^{-9b}	0.383 ^b

Raman spectra, in combination with the XRD results, clearly demonstrate that all ZnO samples grown for various growth times have the hexagonal wurtzite structure, with no indications of impurities.

Fig. 3a–e illustrate SEM images of ZnO nanowires' arrays deposited by ASG on Corning glass substrates, pre-coated with 1× ZnO seed layer, for 2, 5, 10, 24, and 48 h, respectively. As it can be observed, in all cases, the substrates were covered with quite dense and uniform ZnO nanowires' arrays. These nanowires emerge perpendicular to the substrate applied, with almost no nanowires tilted from the surface, while they all display a hexagonal cross-section. These remarks are in agreement with the XRD results, which clearly demonstrate that the ZnO samples deposited by ASG on amorphous ZnO seeded Corning glass substrates exhibit the wurtzite hexagonal crystal structure, showing a preferential growth orientation along the (002) direction (see Fig. 1). It is furthermore observed that the nanowires' diameter remains constant in the range of 150 ± 30 nm despite the growth time, indicating that the control of the diameter is directly related with the grain size of the amorphous ZnO seed layer [23,24]. The length of the ZnO nanowires grown on 1× seeded glass substrates is 500–700 nm for 2 h growth, 1.0–1.2 μ m, 1.2–1.4 μ m, and ~ 1.3 –1.6 μ m for 5 h, 10 h, and 24–48 h growth, respectively. It is therefore concluded that the only parameter that affects the length of the as-grown ZnO nanowires is growth time [23,24,38].

It is worth mentioning that the use of a 3× amorphous ZnO seed layer gives exactly the same diameter and length for the ZnO nanowires as 1× ZnO, implying no significant effect of the number of the amorphous ZnO seed layers on the ZnO nanowires' dimensions. The only noticeable difference between ZnO nanowires on 1× and 3× ZnO seed layer is that the ZnO samples grown on 3× ZnO seeded glass substrates are relatively misaligned compared to the ones on 1× ZnO seed layer (see for example the case of 48 h growth on 3× ZnO seed layer in Fig. 3f), probably due to poor adhesion of the 3× ZnO seed layer itself on the glass substrate, which is currently under further investigation.

Taking into consideration the nanowires' dimensions mentioned above, i.e. their diameter and length, we can estimate their aspect ratio (length over diameter, L/D), which indicates the surface-to-volume ratio of the nanostructured samples. ZnO nanowires grown on both 1× and 3× seed layers for 2 h have an

aspect ratio (L/D) of ~ 5.8 , while L/D becomes ~ 10.0 , ~ 11.7 , and ~ 13.3 for the cases of 5 h, 10 h, and 24–48 h, respectively.

If we associate the SEM images of the as-grown ZnO nanowires with their geometrical features, we could state that the sample with the best orientation along the c-axis, is the one grown on 1× ZnO seed layer for 5 h at 95 °C (see Fig. 3), which has a considerable aspect ratio of ~ 10.0 , (see Fig. 3b).

The optical transmittance spectra of the ZnO nanowires' arrays in the wavelength region 190–990 nm are presented in Fig. 4. All the samples are highly transparent in the visible regime and exhibit a sharp absorption band in the UV region. The presence of an excitonic peak at ~ 350 nm is attributed to a minimum strain and very good crystalline quality of the ZnO samples grown via ASG at 95 °C [39]. It can be noted that increasing growth time from 2 to 48 h leads to a decrease in transmittance. This reduction in the transmittance can be assigned to an increase of the samples' thickness, in agreement with the SEM results, which clearly demonstrate that the ZnO nanowires' length increases with growth time.

ZnO nanowires grown for 2 h on 1× ZnO seed layer exhibit $\sim 88\%$ transmittance at 600 nm, while the corresponding transmittance value for the case of 2 h on 3× ZnO seed layer is $\sim 80\%$ (see Fig. 4). Furthermore, 5 h growth on 1× ZnO and 3× ZnO seed layers gives a transmittance of $\sim 84\%$ and $\sim 72\%$ at 600 nm, respectively. The less transparent ZnO nanowires' arrays samples are those grown for 48 h; 48 h growth on a 1× ZnO seed layer leads to $\sim 59\%$ transmittance at 600 nm, while the corresponding transmittance value for the 48 hr growth on 3× ZnO seed layer is $\sim 49\%$.

3.2. Photocatalytic activity of ZnO nanowires

Fig. 5 presents the normalized integrated area vs. irradiation time curves for ZnO nanowires fabricated by ASG for 2–48 h, on both 1× and 3× seed layers. It can be noticed that all ZnO samples grown on 1× ZnO seed layer show better photocatalytic activity than the ones grown on 3× ZnO seed layer, degrading stearic acid by even 90% at 60 min. This is most probably due to their better orientation along c-axis and thus their larger effective surface area. It is also noticeable that ZnO nanowires grown for 2–10 h are more efficient in terms of photocatalysis than those grown at higher deposition times, probably once more, due to their enhanced orientation. For comparison reasons, the photolysis curve (no catalyst present) is

also displayed in Fig. 5 (black solid squares). It can be seen that the UV light results only in ~7.84% and ~22.02% degradation of SA after 30 and 90 min of exposure, respectively.

The photocatalytic activity of the amorphous ZnO stand-alone seed layers and nanowires' arrays at 30 min is summarized in Table 1, where the stearic acid disappearance rate (mol/min) and the formal quantum efficiency (FQE) are also displayed, following the methodology explained by Mills and Wang [40]. It can be observed that ZnO samples deposited on 1 × ZnO seed layer show better activity than those grown on 3 × ZnO. This is possibly due to better orientation along the *c*-axis, as already discussed in [23,24] (see also Fig. 3).

In fact, ZnO nanowires grown via ASG at 95 °C for 5 h on Corning glass substrates pre-coated with 1 × ZnO seed layer show by far the best photocatalytic activity and FQE, degrading SA by almost 80.44% at 30 min ($\text{FQE} = 5.9 \times 10^{-3}$). This is attributed to the enhanced orientation of the ZnO nanowires grown for 5 h along the *c*-axis (see Fig. 3), together with their high aspect ratio ($L/D \sim 10.0$). Furthermore, the ZnO samples that give the worst photocatalytic activity are the ones grown on 3 × ZnO seed layer for 48 h (13.62% at 30 min, $\text{FQE} = 0.38 \times 10^{-3}$), since they consist of the most reclined and misaligned ZnO nanowires as already seen in Fig. 3f.

It is worth mentioning that the photocatalytic activity tests were carried out for at least five times on our ZnO samples in order to examine their stability under UV illumination, demonstrating no changes in the photocatalytic activity after five runs.

3.3. Wettability properties of ZnO nanowires

Fig. 6(a), (c), (e), (g), and (i) shows wetting angle images for non-irradiated as-deposited ZnO nanowires' arrays on 1 × ZnO for 2–48 h at 95 °C, while in Fig. 7 the corresponding contact angles of the structures are presented.

It is well known that the surface free energy and the surface roughness as well as the vapour contact area play very important roles in the wetting behavior. In the Wenzel model [2], the water drop is assumed to wet the entire rough surface, not leaving any air pockets. Then, the observed water contact angle, θ_w , is given by the following equation:

$$\cos \theta_w = r \cos \theta \quad (1)$$

where r is the ratio of the unfolded surface to the apparent area of contact under the droplet and θ is the contact angle on a flat surface of the same nature as the rough one. Since r is always greater than unity, this model predicts that the contact angle of a liquid that wets a solid ($\theta < 90^\circ$) decreases when its surface is roughened ($\theta_w < \theta$), while, roughening a non-wetting flat surface ($\theta > 90^\circ$) always increases its hydrophobicity ($\theta_w > \theta$). Therefore, the Wenzel's model predicts enhancement of either nonwetting or complete wetting with increasing roughness. In contrast, Cassie and Baxter [41] assumed that the liquid does not completely permeate the roughened solid. As a result, air pockets are trapped inside the features underneath the liquid, which sits above a composite surface made of solid and air. For a Cassie–Baxter drop, the contact angle, θ_{CB} , is an average between the value on air (i.e. 180°) and on the flat solid (i.e. θ) and is given by:

$$\cos \theta_{CB} = -1 + f(1 + \cos \theta) \quad (2)$$

where f defines the fraction of the projected solid surface that is wet by the liquid. As f is always lower than unity, this model always predicts enhancement of hydrophobicity only, independent of the value of the initial contact angle θ . In summary, it can be anticipated that the complete wetting predicted by Wenzel's equation will occur only if the surface texture can be completely penetrated by the volume of the deposited droplet [42].

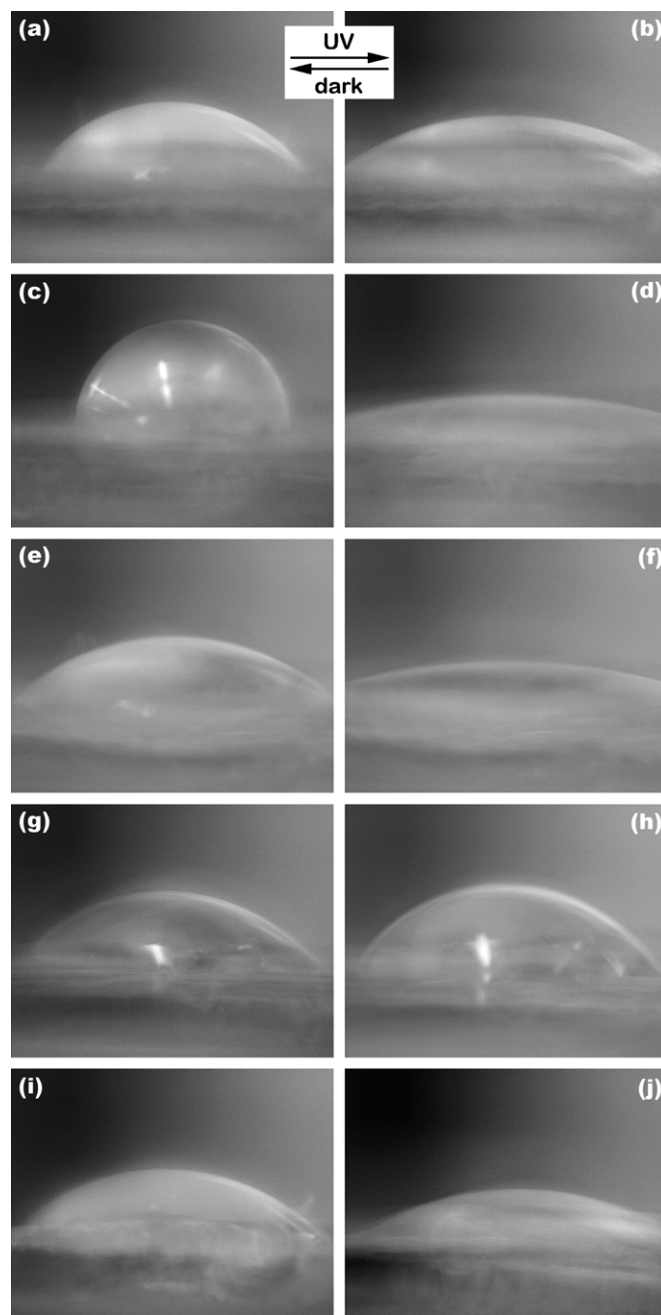


Fig. 6. Water contact angle photographs for as-deposited and UV-treated ZnO nanowires grown on Corning glass substrates pre-coated with 1 × ZnO seed layer before and after illumination for (a) and (b) 2 h; (c) and (d) 5 h; (e) and (f) 10 h; (g) and (h) 24 h and (i) and (j) 48 h growth, respectively.

It can be seen from Fig. 6(a), (c), (e), (g), and (i) that ZnO nanowires' arrays grown on 1 × ZnO seed layer for 5 h (Fig. 6c) show the largest water contact angle (~84°), indicating hydrophobic nature, which may be attributed to the low surface free energy and the high surface area fraction of vapour trapped in between the nanowires, while for growth periods of 2 h and 10–48 h the angle reduces to 47° and 43–52°, respectively. ZnO nanowires grown for 5 h give the largest water contact angle, probably due to their enhanced orientation along the *c*-axis, while as the nanowires recline on the seeded glass substrates, the water contact angle becomes significantly smaller. The decreasing trend of the contact angle for the reclined ZnO nanowires (24, 48 h growth), which have a relatively larger space between them, is consistent with the

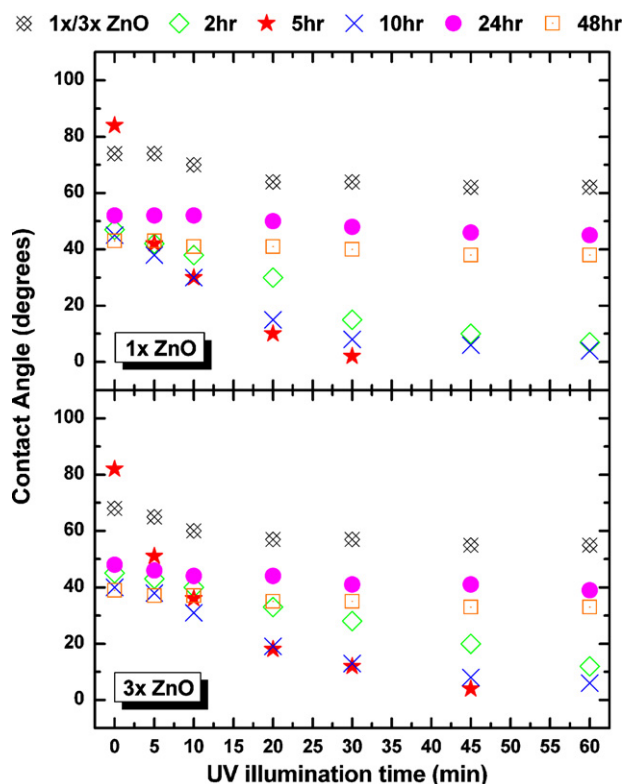


Fig. 7. Variation of the water contact angle of the ZnO nanowires grown by aqueous solution growth for 2–48 h on Corning glass substrates pre-coated with 1× (top) and (bottom) 3× ZnO seed layer, respectively. For comparison reasons, the water contact angles of the 1× and 3× ZnO seed layer are also presented.

Wenzel's model, since this is the only one predicting a decrease of the contact angle with increasing roughness.

Regarding the light-induced modification of the wettability of the as-grown ZnO nanowires, Fig. 6(b), (d), (f), (h), and (j) present the wetting angle images after 20 min of UV irradiation. The corresponding contact angle measurements versus UV illumination time are presented in Fig. 7. As one can see, the well-oriented ZnO nanowires grown for 2, 5, and 10 h exhibit significant photo-induced change in their wettability (see Fig. 7 at 60 min). In particular, ZnO nanowires' arrays grown on 1× ZnO seed layer for 5 h exhibit the most remarkable photo-induced transition to super-hydrophilicity, reaching a nearly zero contact angle (2°) in short time (30 min). The efficiency of these changes is quite remarkable and similar to that observed in ZnO coatings produced by more complicated methods [4]. It should be emphasized that these wettability changes are reversible, since dark storage reconverts the super-hydrophilic surfaces to their original states.

As far as it concerns the origin of the photo-induced hydrophilicity, it has been reported [4] that UV irradiation can generate electron–hole pairs in the ZnO surface, some of the holes reacting with lattice oxygen to form surface oxygen vacancies. Meanwhile, water and oxygen may compete to dissociatively adsorb on these vacancies. The defective sites are kinetically more favorable for hydroxyl adsorption than oxygen adsorption. As a result, the surface hydrophilicity is improved, and the water contact angle can significantly be reduced. It has also been demonstrated that the surface becomes energetically unstable after the hydroxyl adsorption. Since the oxygen adsorption is thermodynamically favored, it is more strongly bonded on the defect sites than the hydroxyl group [4]. Therefore, the hydroxyl groups adsorbed on the defective sites can be replaced gradually by oxygen atoms when the UV-irradiated samples are placed in the dark. Subsequently, the

surface evolves back to its original state (before any UV irradiation), and the wettability is reconverted.

Regarding the ZnO nanowires grown for 24 and 48 h, which did not exhibit any considerable photo-induced change of the water contact angle, this is possibly due to their poor orientation along *c*-axis; These ZnO surfaces with many grooves between individual rods give such a roughness which is insufficient to repel water droplets because of the high surface polarity that makes the water fill the grooves very easily through capillary interaction [43]. Moreover, the subsequent significant reduction of the number of photo-active defect sites, which are in contact with the water molecules, results in the observed limited UV-induced hydrophilicity.

It has been finally observed that ZnO nanowires deposited on 1× ZnO seed layer show better photo-induced changes in their wettability upon UV illumination than those grown on 3× ZnO (Fig. 7, bottom). This is possibly due to better orientation along the *c*-axis, as already seen in Fig. 3e and f.

After storing the samples in dark at RT for 7 days, it was found that they fully recovered to their original hydrophobic state. This procedure was repeated for at least 5 times showing no changes in the hydrophobic to hydrophilic transition of our samples.

4. Conclusions

ZnO nanowires, highly oriented along *c*-axis, were grown from an aqueous solution on glass substrates pre-coated with amorphous ZnO seed layers. To the best of our knowledge, this is the first report of ZnO nanowires' arrays deposited using this type of approach, in which none of the growth steps (ZnO seeding procedure and ZnO nanowires growth) exceeds 95 °C.

The ZnO nanowires emerge perpendicular to the substrate applied, with almost no nanowires tilted from the surface, while their diameter remains constant in the range of 150 ± 30 nm despite the growth time, indicating that the control of the diameter is directly related to the grain size of the amorphous ZnO seed layer. All ZnO samples show remarkable photocatalytic activity regarding the degradation of stearic acid. Among ZnO samples, the one grown on 1× ZnO seed layer for 5 h shows better photocatalytic activity and FQE, degrading stearic acid by 82.16% at 30 min ($\text{FQE} = 5.9 \times 10^{-3}$), due to the much better orientation of the ZnO nanowires along the *c*-axis together with their high aspect ratio. In addition, the surface wettability of the ZnO nanowires was studied. Before irradiation, all well-oriented samples (2–10 h growth) are intrinsically hydrophobic, while they exhibit a significant photo-induced change in their wettability. Once more, ZnO nanowires' arrays grown on 1× ZnO seed layer for 5 h exhibit a remarkable reversible photo-induced transition to super-hydrophilicity after exposure to UV light, reaching a nearly zero contact angle in short time (2° in 30 min). The combination of the effective photocatalytic and wettability properties mentioned above makes the ZnO nanowires grown on 1× amorphous ZnO seed layer for 5 h a good candidate for self-cleaning applications.

We conclude that the ASG method can be employed to control the structural and morphological properties of ZnO nanowires at low temperatures (95 °C), resulting in efficient self-cleaning properties. The next challenge will be to demonstrate that this approach works on a much larger scale, which is significant for future industrial applications.

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