

Article

Photocatalytic Activity and Stability of Porous Polycrystalline ZnO Thin-Films Grown via a Two-Step Thermal Oxidation Process

James C. Moore ^{1,*}, Robert Louder ¹ and Cody V. Thompson ^{1,2}

¹ Department of Chemistry and Physics, Coastal Carolina University, Conway, SC 29528, USA; E-Mails: rklouder@g.coastal.edu (R.L.); cvthomps007@gmail.com (C.V.T.)

² Research & Development Laboratory, Wellman Engineering Resins, Johnsonville, SC 29555, USA

* Author to whom correspondence should be addressed; E-Mail: moorejc@coastal.edu; Tel.: +1-843-349-2985; Fax: +1-843-349-2841.

Received: 29 May 2014; in revised form: 8 August 2014 / Accepted: 12 August 2014 /

Published: 15 August 2014

Abstract: The photocatalytic activity and stability of thin, polycrystalline ZnO films was studied. The oxidative degradation of organic compounds at the ZnO surface results from the ultraviolet (UV) photo-induced creation of highly oxidizing holes and reducing electrons, which combine with surface water to form hydroxyl radicals and reactive oxygen species. Therefore, the efficiency of the electron-hole pair formation is of critical importance for self-cleaning and antimicrobial applications with these metal-oxide catalyst systems. In this study, ZnO thin films were fabricated on sapphire substrates via direct current sputter deposition of Zn-metal films followed by thermal oxidation at several annealing temperatures (300–1200 °C). Due to the ease with which they can be recovered, stabilized films are preferable to nanoparticles or colloidal suspensions for some applications. Characterization of the resulting ZnO thin films through atomic force microscopy and photoluminescence indicated that decreasing annealing temperature leads to smaller crystal grain size and increased UV excitonic emission. The photocatalytic activities were characterized by UV-visible absorption measurements of Rhodamine B dye concentrations. The films oxidized at lower annealing temperatures exhibited higher photocatalytic activity, which is attributed to the increased optical quality. Photocatalytic activity was also found to depend on film thickness, with lower activity observed for thinner films. Decreasing activity with use was found to be the result of decreasing film thickness due to surface etching.

Keywords: ZnO; photocatalysis; Rhodamine B; zinc oxide; self-cleaning; antimicrobial

1. Introduction

Zinc oxide (ZnO) is a highly useful and practical wide bandgap semiconducting material with a broad range of applications, including self-cleaning and anti-fogging surfaces, sterilization, gas sensing, energy production and environmental purification [1–4]. Specifically, ZnO efficiently absorbs ultraviolet (UV) light and has surface electrical properties sensitive to the environment at the interface, with device applications that include gas sensors, photovoltaic cells, light emitting diodes and photocatalysts [1,5–10]. The photocatalytic effects of ZnO are being exploited for use within self-cleaning paints, in environmental remediation applications and prophylactics with nanoparticle and colloidal suspensions demonstrating high photodegradation efficiency for organic compounds [11]. Thin films have received recent interest due to their reusability and transparency, which is essential for applications, such as self-cleaning glass and antimicrobial coatings on solid surfaces and flexible plastics [12–14]. Transparent ZnO films could also find use as fingerprint-resistant barriers on touch screen devices, such as cell phones and tablet computers.

Many environmental pollutants are organic in nature, and many proposed methods of environmental decontamination involve oxidation of the organic pollutants [15]. However, using semiconductor photocatalysts to oxidize and remove such pollutants from the local environment has many advantages over alternative methods [16]. ZnO materials in particular are nontoxic and present little additional harm to the environment in which they are used, contrary to most other methods of decontamination. However, there is some concern about the dissolution of ZnO particles and resulting Zn toxicity in marine environments [4,17]. Furthermore, ZnO photocatalysts do not need to be re-activated after undergoing photoinduced oxidation and reduction reactions. Conversely, activated carbon, a popular choice for water purification, requires expensive and potentially polluting reactivation [18].

Another traditional means of decontamination involves microorganisms, such as bacteria, which biologically degrade toxic organics [18]. However, these processes occur at a much slower rate compared to photocatalytic oxidation by semiconductors, such as ZnO, and are inefficient at concentrations below parts-per-million (ppm) levels, while ZnO photocatalysts have been shown to oxidize pollutants present in extremely low concentrations. Additionally, many pollutants can also be toxic to the microorganisms themselves, reducing their catalytic activity with time. ZnO photocatalysts degrade most organic pollutants non-selectively, though their stability is a topic of study [19].

Extensive work has gone into investigating the photocatalytic properties of ZnO nanoparticles and colloid suspensions [20,21]. For environmental remediation purposes, nanoparticle powders are particularly effective, since they can be readily mixed with the contaminated solution and have a high surface area. However, separating the catalyst from solution is challenging, which makes their use in these applications potentially cost-prohibitive [22]. As mentioned, Zn toxicity is also a concern for these systems, especially if allowed to remain in the environment. Fujishima *et al.* suggest that the nanofilm

form of these semiconductors is preferable to particles for use in fluid decontamination exactly because the nanoparticles need to eventually be collected and removed from the fluid [23,24].

There has been little discussion in the literature concerning the sorts of structural and photophysical properties that can directly affect photocatalytic activity for film-based catalysts. As an example, whether degradation occurs predominantly due to reaction with free-radicals or directly with the holes themselves is controversial, with some groups even proposing a predominant electron-based catalytic pathway on ZnO single-crystal surfaces [23,25]. For surface-based applications, challenges exist with nanoparticle-based films, such as adhesion and optical transparency [26]. Nanoparticles do have a high surface area per volume, which increases the number of available surface states to serve as reaction sites. However, increased crystallinity associated with larger particle sizes typically results in greater optical efficiency and, therefore, higher electron-hole pair production efficiency [23,27,28]. Many applications of decontamination using semiconductor photocatalysts involve the Sun as a practical source of UV illumination, although only 2%–3% of solar radiation will induce semiconductor-catalyzed oxidation [29]. Accordingly, the photodegradation efficiencies of the semiconductor photocatalysts designed for these uses need to be optimized in order to be of practical use. Both high surface area and optical efficiency are required for high photocatalytic activity with metal-oxides. For TiO₂ and ZnO thin, polycrystalline films, a decrease in grain size typically results in increased surface roughness and surface area; however, small grain size typically also corresponds to an increase in deep-level defects that lower the number of photo-induced holes at the surface available for catalysis [28]. These competing mechanisms must be balanced.

In previous work, we have found that thin (<200 nm) ZnO films grown via thermal oxidation of Zn-metal at relatively low temperature (300 °C) result in high surface roughness with low deep-level defects [14,28]. Increasing surface-level Zn interstitials could also result in greater catalytic activity and a favorable shift in wavelength into the visible spectrum. We have also found that significant blue emission associated with Zn interstitials near the surface and very little deep-level emission from bulk-related defects can be obtained via tailoring of the films thickness and grain size, resulting in a potential increase in photocatalytic activity due to a favorable balance of features [28,30].

In this study, we measure the photocatalytic activity and stability of thin, polycrystalline ZnO films fabricated on sapphire substrates via direct current (DC) sputter deposition of Zn-metal films, followed by thermal oxidation at several annealing temperatures. In particular, we describe growth parameters that result in highly porous, polycrystalline films demonstrating high surface roughness while simultaneously exhibiting a high excitonic-to-green emission ratio. We also investigate the time-dependent stability of these films.

In Section 2, we describe the process by which films have been fabricated and characterized, and we discuss the method used for determining catalytic activity. In Section 3, we discuss the resulting morphological, structural and optical properties of the fabricated films. In Section 4, we discuss surface catalysis pathways and the reaction kinetic models used to describe the catalytic activity of these films. Finally, in Section 5, we discuss the balance between crystal grain size and the optical efficiency that affects the photocatalytic activity of polycrystalline ZnO films.

2. Experiment

Zinc films were deposited on *c*-plane sapphire substrates via direct current sputter deposition. Metallic Zn targets were obtained commercially and had a purity of 99.99%. Before deposition, substrates were cleaned via immersion in acetone, ultrasonically cleaned in methanol and rinsed in deionized water. The chamber base pressure was maintained between 1.0×10^{-5} and 2.5×10^{-5} mbars. A gate valve between the chamber and the pump was utilized as a throttle to maintain an Ar pressure of approximately 2×10^{-2} mbars. Sputtering power was maintained between 10 and 20 W with the substrate located approximately 10 cm from the sputter source. Deposition times ranged from 15 to 40 min, resulting in film thicknesses between 100 nm and 600 nm as measured via the AFM profile and reflectometry. Thermal oxidation of the Zn metal films was carried out in an air-ambient muffle furnace. For all samples, Zn films were initially annealed at 300 °C for 9–24 hours to ensure complete oxidation. Some films were then re-annealed for 1 hour at 600 °C, 900 °C and 1200 °C.

Zinc oxide films were characterized via X-ray diffraction (XRD), atomic force microscopy (AFM) and photoluminescence (PL). Structural properties of the ZnO films were measured using Cu-K α radiation in the range from 30° to 50°. The morphology of the films was determined via dynamic-mode AFM using an Anfattec Level AFM and approximately 300 kHz resonant aluminum backside silicon tips. Photoluminescence spectra were obtained at room temperature using a HeCd laser as an excitation source and a power of $P = 0.3 \text{ W/cm}^2$. UV illumination was provided by a deuterium lamp.

Following morphological and optical characterization, the photocatalytic activities of the films were characterized by measuring the degradation of Rhodamine B dye (rhoB) in solution. RhoB was used to simulate an organic environmental contaminant, because its concentration in solution can be accurately measured spectrophotometrically. Oxidized rhoB products do not absorb visible light, so the concentration and the resulting absorbance of the rhoB solutions decrease as the rhoB is oxidized by the ZnO photocatalysts. The overall photocatalytic activities of the materials therefore correlate to the rate of change in the concentration of the rhoB solutions as measured by UV-Vis spectrophotometry.

The UV-Vis spectrophotometer was first calibrated in order to determine the relationship between absorbance measurements and rhoB concentrations. This was accomplished by measuring the absorbance of known concentrations of rhoB and constructing a calibration curve from the resulting measurements (not shown). The concentrations in the rest of the experiment were then calculated from the absorbance measurements. The linear range of the absorbance-concentration relationship was determined to be between 1 and 8 ppm rhoB, so an initial concentration of 8 ppm rhoB in solution was used for the photodegradation experiments.

Each ZnO thin film was incubated in an 8 ppm rhoB solution while irradiated with UV light at a constant power density of 80 $\mu\text{W/cm}$. The absorbance of the solution was taken after 10, 20, 30, 45, 60, 90, 120, 150 and 180 min of UV irradiation at the peak absorbance wavelength (553 nm) for maximum sensitivity, and the corresponding rhoB concentration was calculated using the equation of the rhoB calibration curve. In order to account for differences in the surface areas of the films, the total change in concentration of rhoB at each time interval was divided by the specific surface area of the film and plotted against the time of UV irradiation.

3. Film Growth and Characterization

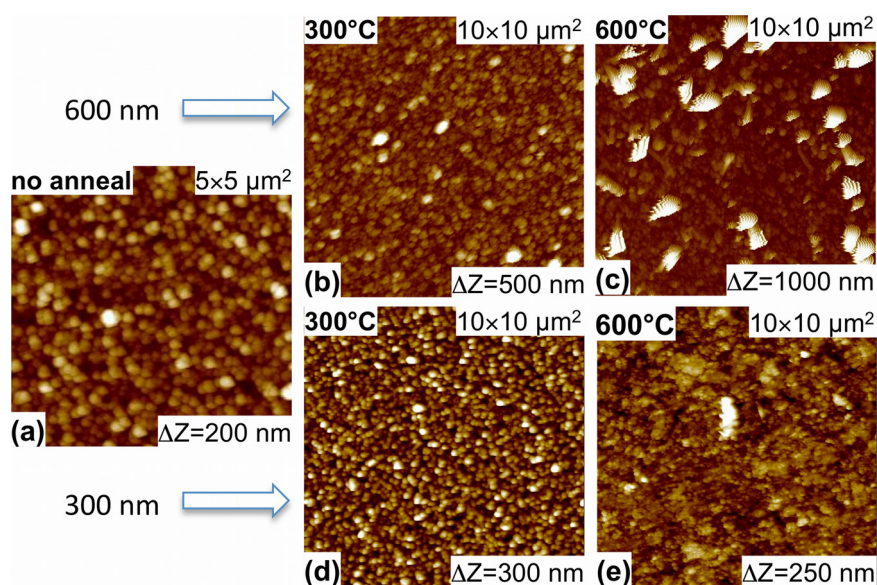
As described earlier, greater catalytic activity is expected with high surface roughness and high optical efficiency. In this section, we discuss the morphology, structure and optical properties of the ZnO thin films under study. Specifically, we describe the morphological and structural evolution with annealing temperature and film thickness, concentrating on crystal grain sizes and surface roughness. We also describe how growth parameters affect the optical properties of the films. In particular, we discuss the relative excitonic emission efficiency and yellow-green band emission.

3.1. Morphology and Structure

The evolution of the surface morphology with increasing annealing temperature for 200 nm- and 600 nm-thick ZnO films is shown in the AFM images presented in Figure 1a–e. As shown in Figure 1a, the as-grown zinc film demonstrates a high surface roughness and approximately 100-nm diameter protrusions. Figure 1b,c shows the surface morphology of resulting 600 nm-thick ZnO films annealed at 300 °C and 600 °C. Figure 1d,e shows the surface morphology of the resulting 200 nm-thick ZnO films annealed at 300 °C and 600 °C. For both thicknesses, there is very little change in the underlying characteristics between zinc-metallic films and ZnO films annealed at 300 °C; however, surface roughness is observed to increase, and protrusions grow in size by approximately 50 nm. This is consistent with previous studies, where Gupta *et al.* show that the preferred orientation of ZnO thermally oxidized on glass can depend on the Zn film texture and oxidizing agent [31]. For 600 nm-thick films, an increase in surface roughness is observed with increasing temperature (Figure 1b,c). Interestingly, at temperatures above 600 °C and a thickness of 600 nm, long vertically-aligned nanorods are visible, which is consistent with previous studies [32]. For a 200 nm-thick films, a decrease in protrusion diameter and surface roughness is observed with increasing temperature (Figure 1d,e). Nanorods are not seen for the thinner films annealed at any temperature. For both film thicknesses, there is little change in surface morphology observed at higher temperatures (not shown). Specifically, the protrusion size does not significantly change.

Grain size was characterized by both AFM and XRD. For films having thicknesses between 400 nm and 600 nm, grain size was observed to increase with increasing annealing temperature from 300 °C to 1200 °C. Interestingly, for films having thicknesses between 100 nm and 200 nm, grain size decreased with increasing temperature up to a certain point. Figure 1d,e shows a decrease in the protrusion diameter from approximately 150 nm to approximately 100 nm at annealing temperatures of 300 °C and 600 °C, respectively, with no further significant change in size as the temperature was further increased. Grain size, as determined by the full width at half maximum in the XRD spectra (not shown), was also found to decrease with increasing temperature up to 600 °C, with relatively small increases at higher temperatures, which is consistent with AFM measurements. This observation appears inconsistent with some reports in the literature for thermally-oxidized ZnO films [33,34]. This discrepancy may be the result of differences in studied temperature regimes, the variations in film thickness and/or our two-step thermal annealing process, where metallic zinc films are all initially oxidized at low temperature. Furthermore, our metallic zinc films display a significantly different texture and larger initial particle size in comparison to films grown via other methods, which has been shown to affect resulting film morphology and structure [31].

Figure 1. AFM topography images of (a) Zn-metal films before oxidation (grayscale range = 200 nm) and the resulting polycrystalline ZnO films after annealing in ambient air; Six hundred nanometer-thick films annealed at (b) 300 °C (grayscale range = 500 nm) and (c) 600 °C (grayscale range = 1000 nm). Two hundred nanometer-thick films annealed at (d) 300 °C (grayscale range = 300 nm) and (e) 600 °C (grayscale range = 250 nm).



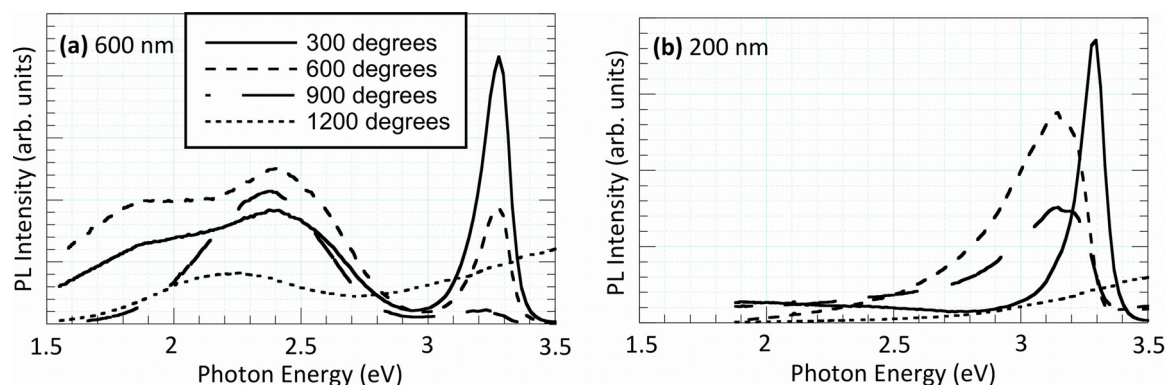
3.2. Optical Properties

Figure 2 shows the PL spectra of ZnO films with a thickness of (a) 600 nm and (b) 200 nm thermally annealed at various temperatures. The spectra for the 600 nm-thick films all show asymmetric broad bands in the yellow-green region, with no significant yellow-green emission observed for the 200 nm-thick films. For all thicknesses, a more narrow band in the UV is observed, which is associated with excitonic emission; however, the 200-nm film demonstrates an asymmetric and broad band in the blue-UV region at higher temperatures. For all thicknesses, the strongest UV excitonic emission is observed at low temperature, with decreasing UV emission observed with increasing annealing temperature. Interestingly, for thinner films, increasing temperature results in a significant redshift (0.15 eV) in the UV excitonic peak and an asymmetrical peak broadening. This change in UV peak position could be explained by a corresponding shift in bandgap energy, which would be consistent with transmission studies of ZnO films grown via the sol-gel method and previous studies of thermally annealed Zn films [28,35]. Wu *et al.* and Dijken *et al.* both demonstrate that an increase in particle size should result in a redshift in energies, which appears inconsistent with our results, since in this temperature and thickness regime, we see a decrease in grain size [36,37]. However, these studies discuss systems where quantum size effects become relevant, and the particle sizes in this study are sufficiently large, such that the shift in bandgap cannot be explained via a similar mechanism. Jain *et al.* speculate that this red shift is the result of an increase in interstitial zinc atoms, which we demonstrated to be the case in a previous study [28,35].

As shown in Figure 2, 600 nm-thick films demonstrate increasing yellow-green band intensity with increasing annealing temperature when compared to UV emission. This can be attributed to a rapid

increase in V_o^+ and O_i^- ion centers at high temperatures [34,36]. In contrast, 200 nm-thick films demonstrate little green and yellow band emission at any temperature (Figure 2b). Deep level emission is attributed to bulk defects; therefore, it is possible that decreased bulk volume results in the formation of relatively fewer deep-level states. If green and yellow emission results from the recombination of a delocalized electron close to the conduction band with a deeply trapped hole in the V_o^+ and O_i^- centers in the bulk, respectively, then a decrease in film thickness would decrease the bulk with respect to the depletion region, resulting in weaker bulk-related, deep-level emission [36]. Reaction kinetics could also contribute, with thinner films having shorter diffusion paths for reactive oxygen species during oxidation [38]. Thin films would therefore demonstrate fewer V_o^+ and O_i^- ions at any annealing temperature, as observed.

Figure 2. PL spectra of ZnO films grown at 300 °C, 600 °C, 900 °C and 1200 °C at thicknesses of (a) 600 nm and (b) 200 nm. For thicker films, increasing green band emission relative to UV emission is seen with increasing temperature. Thinner films demonstrate little green band emission; however, a significant redshift in UV emission and asymmetrical band broadening is observed at higher temperatures.



For thin films at high temperatures, the asymmetric and broad UV excitonic emission bands result from increasing blue emission and corresponding decreasing UV emission [28]. As shown in Figure 2b, the PL spectra for the 200 nm-thick film exhibited the most dramatic blue band emission and very low green band emission at all temperatures. Wang *et al.* found that the intensities of the green and yellow cathodoluminescence peaks were strongly affected by the width of the free-carrier depletion region near the surface [34]. They argue that single ionized oxygen vacancies exist only in the bulk, so the magnitude of the depletion region in relation to the bulk directly affects the intensity of the green emission in the cathodoluminescence spectrum. It has been suggested that blue emission results from zinc interstitials found in the depletion region, so an approximately 400-nm blue emission should only be observed in a sample with a wide depletion region relative to the bulk. Otherwise, deep-level green emission will dominate [28,39,40]. Therefore, the emergence of blue emission with decreasing film thickness results from a low ratio of the bulk to the depletion region.

Temperature and grain size also contribute to the PL spectra, since no blue emission is observed for 200-nm films annealed at 300 °C (see Figure 2b). As discussed, we observe a larger grain size via XRD and AFM for 200-nm films annealed at 300 °C, resulting in a larger bulk to depletion region ratio, which could contribute to the weaker blue emission. Furthermore, thinner films have shorter diffusion paths for

reactive oxygen species during oxidation, and lower temperatures slow the Zn/O₂ reaction. This results in fewer zinc interstitials, which would manifest as weaker blue emission and a red shift in both blue and UV emissions, as is observed.

For photocatalysis applications, thin ZnO films show significant promise due to their potential for balancing high optical quality with high surface roughness. In particular, 200 nm-thick films annealed at low temperature (300 °C) demonstrate a high UV-to-green emission ratio with relatively high surface roughness. Low-temperature annealed 600-nm thick films also show strong excitonic photoemission combined with a tall protrusion height within the porous film structure, which could result in greater effective surface area for photochemical reactions. In this study, we investigate photocatalysis with these thin films, because they show the most promise for high photocatalytic activity.

4. Surface Catalysis and Reaction Kinetics

Metal-oxide semiconductors use light energy to catalyze oxidation-reduction reactions via electron-hole pair production at the material surface [41,42]. The photogenerated holes on the semiconductor surface have a high oxidation potential, while the photogenerated electrons have a high reduction potential [19,23]. Several types of aqueous reactions catalyzed by electron-hole pairs lead to the formation of the hydroxyl radicals and reactive oxygen species that are directly responsible for the oxidative degradation of organic compounds. One of these reactions involves the oxidation of water (H₂O) by a hole (h⁺) into hydrogen ions (H⁺) and a hydroxyl radical (O^{*}):



Another reaction involves the reduction of molecular oxygen (O₂) into a superoxide radical (O₂^{−*}) by a photogenerated electron (e[−]):



The superoxide radical can be further reduced by another electron and then paired with two H⁺ ions to form hydrogen peroxide (H₂O₂):



The hydrogen peroxide can then be reduced by an electron to form hydroxyl radicals:



By these reactions, either the electrons or the holes of the photogenerated electron-hole pairs can produce hydroxyl and superoxide radicals that can subsequently degrade organic compounds [19,23]. It has also been proposed that the electrons or holes themselves may be responsible for at least some of the degradation of organics. Whether degradation occurs predominantly due to reaction with free-radicals or directly with the holes themselves is controversial, with some groups even proposing a predominant electron-based catalytic pathway on ZnO single-crystal surfaces [23,25]. Most likely, however, a large combination of chemical reactions involving various intermediates ultimately leads to the degradation of the organic compounds, which complicates the mathematical descriptions of the rates at which the overall degradation occurs [19].

Simplified mathematical descriptions of the degradation reactions have been used to experimentally quantify and compare photocatalytic activities. For most purposes, especially when the concentration of the contaminant is less than 10 ppm, the reaction can be considered first order, meaning that the time t rate of change in concentration c of the contaminant, dc/dt , follows the general relationship:

$$-\frac{dc}{dt} = kc \quad (5)$$

where k is the rate constant [19]. This equation has been modified for solid photocatalysts to account for the surface area of the photocatalyst and the intensity of the incident light, as follows:

$$-\frac{dc}{dt} = kcA_S\sqrt{I} \quad (6)$$

where I is the intensity of light used and A_S is the total surface area of the photocatalyst [23]. The solution to this differential equation is as follows:

$$c(t) = c_0 e^{-ktA_S\sqrt{I}} \quad (7)$$

where c_0 is the initial concentration of the contaminant. In order to make the concentration-time relationship linear, the equation can be rewritten as the integrated rate law, as follows:

$$\ln \frac{c}{c_0} = -ktA_S\sqrt{I}. \quad (8)$$

When the natural log of the normalized concentration c/c_0 is plotted as a function of time, the rate constant k can be easily determined from the slope of the linear best-fit. The rate constant is the figure of merit referred to in the literature for quantitative comparisons of photocatalytic activity [19].

Zero- and half-order rate laws have also been used to describe the photocatalyst degradation reactions. In particular, the half-order rate law has been shown to more accurately model photocatalytic reactions on metal-oxide surfaces, most likely due to the combination of zero- and first-order chemical reactions involved in photodegradation [19]. The differential and integrated forms of the half-order rate law are as follows:

$$-\frac{dc}{dt} = A_S\sqrt{I}kt^{1/2} \quad (9)$$

and:

$$c^{1/2}(t) = c_0^{1/2} - A_S\sqrt{I}\frac{k}{2}t \quad (10)$$

respectively. In this study, we calculate $(c^{1/2} - c_0^{1/2})/A_S$ and plot this as a function of the UV irradiation time, with the half-order rate constant determined from the slope of the linear best-fit. While the light intensity is a factor in calculating the rate constant, the same light intensity was used for each experiment in this study, and its effect on the rate of each reaction can be negated.

5. Results

In this section, we discuss the photocatalytic activity of the fabricated ZnO thin films and its dependency on the annealing temperature and film thickness. We also discuss the stability of these films with continued use by investigating the time-dependence of the photocatalytic activity. As

described in Section 3, the annealing temperature and film thickness have been shown to affect both the surface roughness and the efficiency of electron-hole pair production, which have been shown to affect photocatalysis. Furthermore, surface degradation of ZnO with exposure to aqueous environments has been reported, which could affect the long-term stability of ZnO thin films with respect to photocatalysis [4,17].

5.1. Reaction Order

Figure 3a,b shows that concentrations of rhoB fit to the first- and half-order integrated rate law, respectively, for increasing annealing temperature and constant 200 nm-thick films. Half-order reaction kinetics (Equation (10)) better approximate the overall degradation reaction than the more commonly applied first-order rate law (Equation (8)), as indicated by the higher coefficient of determination (R^2) values for the linear fits (shown in Table 1). The orders of the individual reactions that ultimately lead to the degradation of organic compounds, such as rhoB by semiconductor photocatalysts, vary between zero and one, depending on the reaction. When these reactions are coupled, the order of the overall reaction is somewhere between zero and one, and so the best approximation is most likely to be the half-order rate law [19]. For reasons of simplicity and uniformity between studies, the first-order rate law has commonly been applied to quantify the photocatalytic activities of semiconductor photocatalysts. However, because the half-order rate law is a better and more logical approximation, the photocatalytic activities were calculated in this study using the half-order integrated rate law (Equation (10)).

Figure 3. Concentrations of rhoB fit to the (a) first order and (b) half-order integrated rate law for varying annealing temperature (300–900 °C). The best fit curves are indicated by the solid lines, with the slope of the best fit curves representing the photocatalytic activity. The control consists of degradation measurements made in the absence of catalyst films.

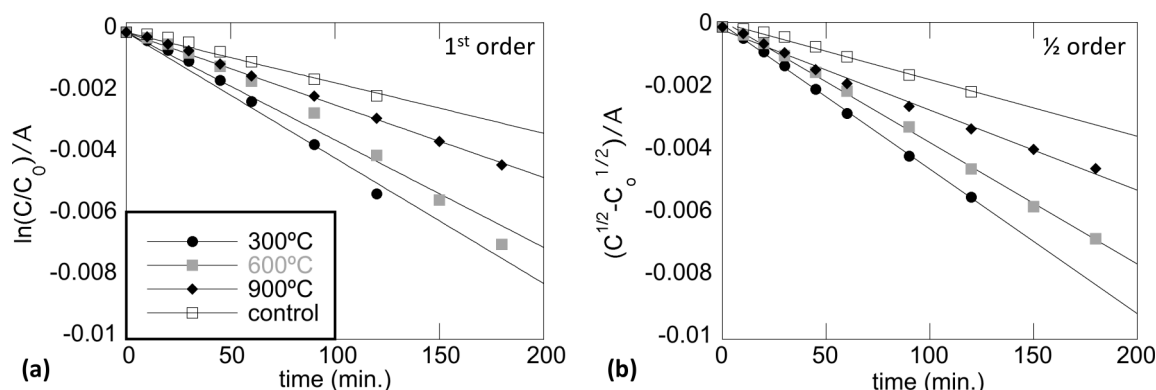
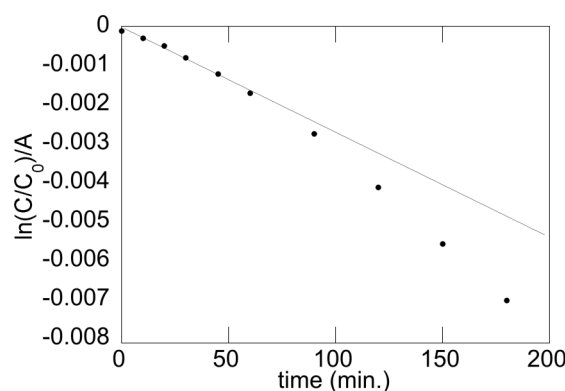


Table 1. Regression statistics for first- and half-order reaction kinetics.

Annealing Temperature (°C)	R^2 1st order	R^2 half-order
300	0.999	0.856
600	0.998	0.887
900	0.993	0.886

However, it should be noted that the order of the overall reaction is determined by which reaction types predominate at any given moment, which itself is dependent on a multitude of factors. One factor that determines the predominant reaction that is taking place at any given moment is the concentration of the various molecules involved in the degradation reactions, which varies significantly over time. The order of the overall reaction can thus change over the course of the photocatalysis experiment due to decreasing concentrations of rhoB or increasing concentrations of free radicals and peroxides in solution. The change in overall reaction order is apparent from inspection of Figure 4, which is a semi-log plot representing the first-order rate law. The semi-log concentration is linear during the first 60 min of irradiation time and significantly non-linear thereafter, suggesting a change in overall reaction order. Therefore, there is a limit to the ability of the reaction to follow any integrated rate law with time, which is not necessarily a result of the catalyst film itself. For studies involving long-term film stability, activities are measured in shorter 60–120-min time intervals before the rhoB solution is replenished.

Figure 4. Semi-log plot of rhoB concentration with time. Within the first 60 min of irradiation, first-order reaction kinetics fit the observed degradation as indicated by the solid line. However, the change in overall reaction order is apparent after the first 60 min.



5.2. Photocatalytic Activity and Annealing Temperature

As shown in Figure 3b, the half-order photocatalytic activity decreases with increasing annealing temperature, as indicated by the decreasing slope of the best-fit lines with increasing temperature. A control measurement was made, which consisted of a sapphire substrate without a ZnO film incubated in an 8-ppm rhoB solution, while irradiated with UV light (hollow squares, Figure 3b). We observed no difference in photodegradation between rhoB solutions alone and rhoB solutions with immersed sapphire, suggesting that the substrate plays no significant role in the degradation of the rhoB. It is clear that some degradation of rhoB occurs as a result of UV illumination alone. To determine the contributions to degradation by the ZnO films and, therefore, the photocatalytic activity of the films, we subtract the control curve from measurements made in ZnO-incubated solution, with the resulting slope of the best-fit representing the photocatalytic activity of the metal-oxide films. The photocatalytic activities of 200 nm-thick ZnO films determined from half-order kinetics are reported in Table 2.

The activity of the films annealed at 600 °C was reduced by 20% compared to the films annealed at 300 °C, and the activity of the 900 °C annealed films was reduced by 30% compared to the 600 °C annealed films. Interestingly, this is the same proportional reduction as is observed for peak PL excitation

and annealing temperature, as shown in Figure 2b. This suggests that excitation efficiency, specifically in the excitonic band, can significantly affect the photocatalytic activity of metal-oxide films.

Table 2. Photocatalytic activity at various annealing temperatures.

Annealing temperature (°C)	Photocatalytic activity ($\text{ppm}^{1/2}\text{mm}^{-2}\text{min}^{-1}$)
300	$(57 \pm 1) \times 10^{-6}$
600	$(31 \pm 1) \times 10^{-6}$
900	$(10 \pm 1) \times 10^{-6}$

Since PL excitation is directly correlated to electron-hole pair formation on the semiconductor surface, the films with higher optical quality have higher rates of electron-hole pair formation. Furthermore, the oxidation and reduction reactions that lead to the degradation of rhoB and other organic compounds by the semiconductor photocatalysts are dependent on the availability of electrons and holes on the surface of the semiconductor, so the optical quality of the films is the most important factor in the photocatalyzed degradation by the semiconductor, at least when morphological features are similar.

The effective surface area on the nano-scale should also affect the photocatalytic activities of the films, though the precise extent of its significance has been difficult to determine for metal-oxides due to the connection between optical properties and grain size, surface roughness and other morphological properties [43]. Since the films annealed at 300 °C in this study have larger grain sizes than those annealed at higher temperature, their surface area is effectively smaller, resulting in lower rates of contact with molecules in solution and ultimately leading to potentially lower reaction rates, as well. However, this was not observed, and we speculate that this change in grain size with increasing temperature was too small to have a significant contribution to the photocatalytic activity. Furthermore, there is no observed change in grain size with increasing annealing temperature past 600 °C, while significant reductions in photocatalytic activity are still observed, suggesting that optical properties dominate the contribution to activity in this case.

5.3. Photocatalytic Activity and Film Thickness

Figure 5a shows the half-order concentration curves for films annealed at 300 °C and having thickness varying from 200 to 600 nm. Again, a control measurement was made, which consisted of a sapphire substrate without a ZnO film incubated in an 8-ppm rhoB solution while irradiated with UV light (hollow squares, Figure 5a). We subtracted the control curve from measurements made in ZnO-incubated solution (filled triangles, diamonds, squares and circles in Figure 5a), with the resulting slopes of the best-fit representing the photocatalytic activities of the metal-oxide films. The half-order photocatalytic activities are plotted as a function of film thickness in Figure 5b and are shown in Table 3. An approximately linear increase in photocatalytic activity is observed with increasing film thickness, as shown via the solid line in Figure 5b.

In the previous section, we investigated photocatalytic activity with film annealing temperature while keeping film thickness constant. For increasing annealing temperature, there was a significant decrease in photoemission efficiency, but little change in overall surface morphology, at least with

respect to the observable height of ZnO grain protrusions, as seen in Figure 1d,e. In this section, we discuss the photocatalytic activity as a function of film thickness with constant annealing temperature. A comparison of the excitonic peaks for films annealed at 300 °C at a thicknesses of 600 and 200 nm shows no significant difference in excitonic photoemission efficiency with thickness, as seen in Figure 2a,b, respectively. However, inspection of the AFM images shown in Figure 1b,d indicates a doubling in the observable ZnO grain protrusion height when going from 200 to 600 nm-thick films.

Figure 5. Half-order concentration curves for films annealed at 300 °C and having thicknesses varying from 200 to 600 nm. Data is fit to the half-order integrated rate law, with the curves of best-fit shown as the solid lines.

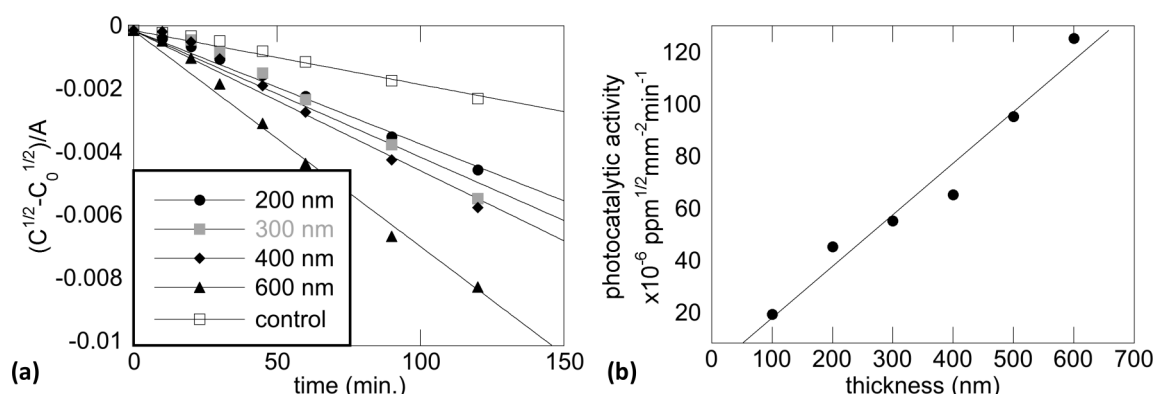


Table 3. Photocatalytic activity at various film thicknesses.

Film thickness (nm)	Photocatalytic activity ($\text{ppm}^{1/2}\text{mm}^{-2}\text{min}^{-1}$)
100	$(21 \pm 1) \times 10^{-6}$
200	$(47 \pm 1) \times 10^{-6}$
300	$(57 \pm 1) \times 10^{-6}$
400	$(67 \pm 1) \times 10^{-6}$
500	$(97 \pm 1) \times 10^{-6}$
600	$(127 \pm 1) \times 10^{-6}$

The significant increase in protrusion height could explain the increase in photocatalytic activity with increasing film thickness. As mentioned, the effective surface area on the nano-scale may also affect the photocatalytic activities of the films, though the precise extent of its significance has been under question [43]. The polycrystalline nature of our films results in approximately 100–150 nm-diameter ZnO columns that protrude upward from the surface, with an inter-column spacing on the order of 10–20 nm. Increasing the height of these columns results in an effective increase in surface area, resulting in higher rates of contact with molecules in solution and ultimately leading to higher reaction rates. The observed increase in green and yellow band emission with thicker films appears to have no effect on the photocatalytic activity of the films. Therefore, as expected, the excitonic photoemission efficiency and effective surface area of the catalytic material are the main contributors to activity. For films grown via a two-step thermal annealing process, low temperature annealing combined with relatively thick films

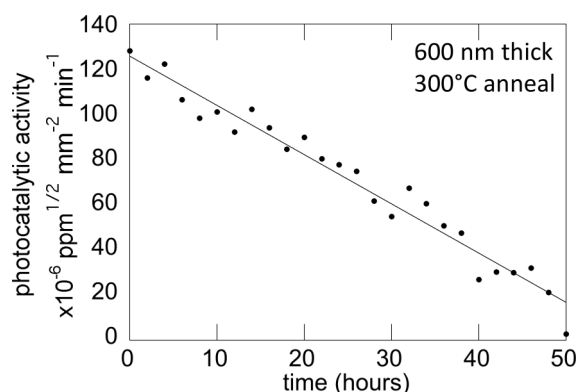
results in materials demonstrating greater photocatalytic activity, due mainly to high optical quality and the porous nature of the morphology.

5.4. Film Stability

To determine film stability, we looked at the evolution of the photocatalytic activity over long periods of time (up to two days of continuous incubation). The order of the overall reaction can change over the course of the photocatalysis experiment due to decreasing concentration of rhoB or increasing concentrations of free radicals and peroxides in solution, which could manifest as a decrease in activity. We are interested in the photocatalytic activity of the films, so activity was determined via rhoB concentration measurements over one-hour intervals. The rhoB solution was replaced after each interval to ensure sufficient concentrations of rhoB and relatively low concentrations of free radicals and peroxides.

Figure 6 shows the photocatalytic activity as a function of time for a ZnO film having a thickness of 600 nm and annealed at a temperature of 300 °C. The photocatalytic activity decreases approximately linearly over 50 hours until reducing to zero. Interestingly, after 50 hours of continued incubation, the morphology of the sample is consistent with the morphology of the sapphire substrate (not shown), suggesting that the cause of the observed decreasing activity is the degradation of the ZnO film. During the incubation period, ZnO at the interface dissociates, forming Zn^+ and O^- ions that leave the film structure and enter the solution. This is consistent with reports in the literature concerning the stability of bulk and thin-film ZnO in contact with aqueous solutions [4,17]. Preferential etching should occur at termination sites, such as at the tips of ZnO grain protrusions seen in Figure 1b. This results in a slow decrease in film thickness as the reactions take place. As shown in the previous section, when the photoemission efficiency is similar, the predominant contributor to the photocatalytic activity is the specific surface area and, in the context of this study, the film thickness. Therefore, the photocatalytic activity decreases with time due to surface etching of the film, resulting in decreasing film thickness.

Figure 6. Photocatalytic activity as a function of time for a ZnO film having a thickness of 600 nm and annealed at a temperature of 300 °C. Measurements were made spectrophotometrically over one-hour increments, with the rhoB solution being replaced after each one-hour measurement.



6. Discussion

Extensive work has gone into investigating the photocatalytic properties of ZnO nanoparticles and colloid suspensions [20]. However, separating the catalyst from solution is challenging, which makes their use in these applications potentially cost-prohibitive [22]. As mentioned, Zn toxicity is also a concern for these systems, especially if allowed to remain in the environment. Fujishima *et al.* suggest that the nanofilm form of these semiconductors is preferable to particles for use in fluid decontamination exactly because the nanoparticles need to eventually be collected and removed from the fluid [23,24]. There has been little discussion in the literature concerning the sorts of structural and photophysical properties that can directly affect photocatalytic activity for film-based catalysts. For the porous polycrystalline films discussed in this study, both optical and morphological properties have been shown to significantly affect the photodegradation of organics at the interface.

Polycrystalline films demonstrating high surface roughness and with small crystal grain size do typically have a high effective surface area, which increases the number of available surface states to serve as reaction sites. The concern with respect to the engineering of effective metal-oxide-based catalysts, though, is that the decreased crystallinity associated with these surfaces typically results in reduced optical efficiency and, therefore, lower electron-hole pair production efficiency [23,27,28]. Both high surface area and optical efficiency are required for high photocatalytic activity with metal-oxides. For TiO₂ and ZnO thin, polycrystalline films, a decrease in grain size typically results in increased surface roughness and surface area; however, small grain size typically also corresponds to an increase in deep-level defects that could lower the number of photo-induced holes at the surface available for catalysis [28]. These competing mechanisms must be balanced. Thermal oxidation of Zn-metal films at low annealing temperatures applied over many hours results in a balance between high effective surface area and optical quality. Furthermore, the porous nature of these films results in increased effective surface area with increased film thickness, without a corresponding decrease in optical quality, at least with respect to electron-hole pair production efficiency.

However, a significant problem with metal-oxide systems, such as ZnO, is long-term stability. The most photoactive films discussed in this study decrease in effectiveness by 50% in approximately 24 hours. There is also some concern about the dissolution of ZnO particles and resulting Zn toxicity in marine environments [4,17]. Although most of the work on ZnO dissolution has been with respect to nanoparticles and colloid suspensions, there is increasing evidence that Zn toxicity should be a concern for film-based systems and even for the interface of the single-crystal bulk [4,25]. Continued work needs to be done to find metal-oxide systems that exhibit high catalytic activity and that are passivated from preferential etching at termination sites, resulting in increased stability.

7. Conclusions

In summary, the photocatalytic activity and stability of thin, polycrystalline ZnO films was studied. The oxidative degradation of organic compounds at the ZnO surface results from the ultraviolet (UV) photo-induced creation of highly oxidizing holes and reducing electrons, which combine with surface water to form hydroxyl radicals and reactive oxygen species. Therefore, the efficiency of electron-hole pair formation is of critical importance for self-cleaning and antimicrobial applications with these

metal-oxide catalyst systems. In this study, the lower annealing temperature of the fabricated ZnO thin films resulted in decreased protrusion size and specific surface area, as well as increased UV excitonic emission. The films oxidized at lower annealing temperatures exhibited higher photocatalytic activity, which is attributed to the increased optical quality. Photocatalytic activity was also found to depend on film thickness, with lower activity observed for thinner films due to a decrease in effective surface area. Decreasing activity with use was found to be the result of decreasing film thickness due to preferential surface etching.

Acknowledgments

This work was supported by the U.S. National Science Foundation Division of Materials Research (NSF-DMR 1104600) and the II-VI Foundation's Undergraduate Research Program. The photoluminescence data presented in this paper were obtained at Virginia Commonwealth University (Richmond, VA, USA) in the laboratory of Mikhail Reshchikov.

Author Contributions

This work was completed in Christopher Moore's research laboratory under his direction. Data collection and analysis was completed by all three authors. Robert Louder contributed writing to Sections 4 and 5. Cody Thompson contributed writing to Section 5. Both Robert Louder and Cody Thompson provided their main contributions to this work while undergraduate students at Coastal Carolina University. Robert Louder is currently a biophysics graduate student at the University of California, Berkeley. Cody Thompson is currently a supervisor in the Research and Development laboratory at Wellman Engineering Resins.

Conflicts of Interest

The authors declare no conflict of interest.

References

1. Ozgur, U.; Alivov, Y.; Liu, C.; Teke, A.; Reshchikov, M.; Dogan, S.; Avrutin, V.; Cho, S.; Morkoc, H. A comprehensive review of ZnO materials and devices. *J. Appl. Phys.* **2005**, *98*, doi:10.1063/1.1992666.
2. Zhao, Q.; Xie, Y.; Zhang, Z.; Bai, X. Size-selective synthesis of zinc sulfide hierarchical structures and their photocatalytic activity. *Cryst. Growth Des.* **2007**, *7*, 153–158.
3. Diebold, U. Structure and properties of TiO₂ surfaces: A brief review. *Appl. Phys. A* **2003**, *76*, 681–687.
4. Moore, J.; Kenny, S.; Baird, C.; Morkoc, H.; Baski, A. Electronic behavior of the Zn- and O-polar ZnO surfaces studied using conductive atomic force microscopy. *J. Appl. Phys.* **2009**, *105*, doi:10.1063/1.3132799.
5. Covington, L.; Moore, J. Photoconductivity and transient response of Al:ZnO:Al planar structures fabricated via a thermal oxidation process. *Thin Solid Films* **2013**, *506*, 106–111.

6. Moore, J.; Thompson, C. A phenomenological model for the photocurrent transient relaxation observed in ZnO photodetector devices. *Sensors* **2013**, *13*, 9921–9940.
7. Ali, G.; Thompson, C.; Jasim, A.; Abdulkaki, I.; Moore, J. Effect of embedded Pd microstructures on the flat-band-voltage operation of room temperature ZnO-based propane gas sensors. *Sensors* **2013**, *13*, 16801–16815.
8. Ali, G.; Kadhim, A.; Thompson, C.; Moore, J. Electrical and optical effects of Pd microplates embedded in ZnO thin film based MSM UV photodetectors: A comparative study. *Sens. Actuators A* **2014**, *209*, 16–23.
9. Moore, J.; Covington, L.; Foster, R.; Gee, E.; Jones, M.; Morris, S. ZnO ultraviolet photodetectors grown via thermal oxidation of Zn-metal on glass and sapphire substrates. *Proc. SPIE* **2011**, *7940*, doi:10.1117/12.873837.
10. Gedamu, D.; Paulowicz, I.; Kaps, S.; Lupan, O.; Wille, S.; Haidarschin, G.; Mishra, Y.K.; Adelung, R. Rapid Fabrication Technique for Interpenetrated ZnO Nanotetrapod Networks for Fast UV Sensors. *Adv. Mater.* **2014**, *26*, 1541–1550.
11. Antoine, T.E.; Mishra, Y.K.; Trigilio, J.; Tiwari, V.; Adelung, R.; Shukla, D. Prophylactic, therapeutic and neutralizing effects of zinc oxide tetrapod structures against herpes simplex virus type-2 infection. *Antivir. Res.* **2010**, *96*, 363–375.
12. Hashimoto, K.; Irie, H.; Fujishima, A. TiO₂ Photocatalysis: A Historical Overview and Future Prospects. *Jpn. J. Appl. Phys.* **2005**, *44*, 8269–8285.
13. You, H.C.; Lin, Y.H. Investigation of the Sol-Gel Method on the Flexible ZnO Device. *Int. J. Electrochem. Sci.* **2012**, *7*, 9085–9094.
14. Moore, J.; Louder, R.; Covington, L.; Stansell, R. Photoconductivity and photocatalytic activity of ZnO thin films grown via thermal oxidation. *Proc. SPIE* **2012**, *8263*, doi:10.1117/12.906227.
15. Oppenlander, T. *Photochemical Purification of Water and Air*; Wiley-VCH: Weinheim, Baden-Württemberg, 2003.
16. Anpo, M. Utilization of TiO₂ photocatalysts in green chemistry. *Pure Appl. Chem.* **2000**, *72*, 1265–1270.
17. Bian, S.; Mudunkotuwa, I.; Rupasinghe, T.; Grassian, V. Aggregation and dissolution of 4 nm ZnO nanoparticles in aqueous environments: Influence of pH, ionic strength, size, and adsorption of humic acid. *Langmuir* **2011**, *27*, 6059–6068.
18. Juan, K. The fundamental and practice for the removal of phenolic compounds in wastewater. *Ind. Pollut. Prev. Control* **1984**, *3*, 88–92.
19. Carp, O.; Huisman, C.; Reller, A. Photoinduced reactivity of titanium dioxide. *Progr. Solid State Chem.* **2004**, *32*, 33–177.
20. Wan, Q.; Wang, T.; Zhao, J. Enhanced photocatalytic activity of ZnO nanotetrapods. *Appl. Phys. Lett.* **2005**, *87*, doi:10.1063/1.2034092.
21. Reimer, T.; Paulowicz, I.; Röder, R.; Kaps, S.; Lupan, O.; Chemnitz, S.; Benecke, W.; Ronning, C.; Adelung, R.; Mishra, Y.K. Single step integration of ZnO nano- and microneedles in Si trenches by novel flame transport approach: Whispering Gallery Modes and photocatalytic properties. *ACS Appl. Mater. Interfaces* **2014**, *6*, 7806–7815.

22. Konstantinou, I.; Albanis, T. TiO₂-assisted photocatalytic degradation of azo dyes in aqueous solution: Kinetic and mechanistic investigations. *Appl. Catal. B* **2004**, *49*, 1–14.
23. Fujishima, A.; Rao, T.; Tryk, D. Titanium dioxide photocatalysis. *J. Photochem. Photobiol. C Photochem. Rev.* **2000**, *1*, 1–21.
24. Chakrabarti, S.; Dutta, B. Photocatalytic degradation of model textiledyes in wastewater using ZnO as semiconductor catalyst. *J. Hazard. Mater. B* **2004**, *112*, 269–278.
25. Yonghao, W.; Feng, H.; Danmei, P.; Bin, L.; Dagui, C.; Wenwen, L.; Xueyuan, C.; Renfu, L.; Lin, Z. Ultraviolet-light-induced bactericidal mechanism on ZnO single crystals. *Chem. Commun.* **2009**, 6783–6785.
26. Fujishima, A.; Zhang, X.; Tryk, D. TiO₂ photocatalysis and related surface phenomena. *Surface Sci. Rep.* **2008**, *63*, 515–582.
27. Lin, D.; Wu, H.; Zhang, R.; Pan, W. Enhanced photocatalysis of electrospun Ag-ZnO heterostructured nanofibers. *Chem. Mater.* **2009**, *21*, 2479–3484.
28. Moore, J.; Covington, L.; Stansell, R. Affect of film thickness on the blue photoluminescence from ZnO. *Phys. Status Solidi A* **2012**, *209*, 741–745.
29. Sakthivel, S.; Kisch, H. Daylight photocatalysis by carbon-modified titanium dioxide. *Angew. Chem. Int. Ed.* **2003**, *351*, 1378–1383.
30. Covington, L.; Stansell, R.; Moore, J. Emergence of blue emission with decreasing film thickness and grain size for ZnO grown via thermal oxidation of Zn-metal films. *Mater. Res. Soc. Proc.* **2012**, *1394*, doi:10.1557/opl.2012.245.
31. Gupta, R.; Shridhar, N.; Katiyar, M. Structure of ZnO films prepared by oxidation of metallic zinc. *Mater. Sci. Semi. Proc.* **2002**, *5*, 11–15.
32. Chen, S.; Liu, Y.; Ma, J.; Zhao, D.; Zhi, Z.; Lu, Y.; Zhang, J.; Shen, D.; Fan, X. High-quality ZnO thin films prepared by two-step thermal oxidation of metallic Zn. *J. Cryst. Growth* **2002**, *240*, 467–472.
33. Cho, S.; Ma, J.; Kim, Y.; Sun, Y.; Wong, G.; Ketterson, J. Photoluminescence and ultraviolet lasing of polycrystalline ZnO thin films prepared by the oxidation of the metallic Zn. *Appl. Phys. Lett.* **1999**, *75*, doi:10.1063/1.125141.
34. Wang, Y.; Lau, S.; Lee, H.; Yu, S.; Tay, B.; Zhang, X.; Hng, H. Photoluminescence study of ZnO films prepared by thermal oxidation of Zn metallic films in air. *J. Appl. Phys.* **2003**, *94*, doi:10.1063/1.1577819.
35. Jain, A.; Sagar, P.; Mehra, R.M. Changes of structural, optical and electrical properties of sol-gel derived ZnO films with their thickness. *Mater. Sci. Pol.* **2007**, *25*, 233–242.
36. Wu, X.; Siu, G.; Fu, C.; Ong, H. Photoluminescence and cathodoluminescence studies of stoichiometric and oxygen-deficient ZnO films. *Appl. Phys. Lett.* **2001**, *78*, doi:10.1063/1.1361288.
37. Van Dijken, A.; Meulenkaamp, E.; Vanmaekelbergh, D.; Meijerink, A. Identification of the transition responsible for the visible emission in ZnO using quantum size effects. *J. Lumin.* **2000**, *90*, 123–128.

38. Aida, M.; Tomasella, E.; Cellier, J.; Jacquet, M.; Bouhssira, N.; Abed, S.; Mosbah, A. Annealing and oxidation mechanism of evaporated zinc thin films from zinc oxide powder. *Thin Solid Films* **2006**, *515*, 1494–1499.
39. Zhao, J.; Hu, L.; Wang, Z.; Zhao, Y.; Liang, X.; Wang, M. High-quality ZnO thin films prepared by low temperature oxidation of metallic Zn. *Appl. Surf. Sci.* **2004**, *229*, 311–315.
40. Zhao, L.; Lian, J.S.; Liu, Y.H.; Jiang, Q. Influence of preparation methods on photoluminescence properties of ZnO films on quartz glass. *Trans. Nonferrous Metals Soc. China* **2008**, *18*, 145–149.
41. Fujishima, A.; Honda, K. Electrochemical photolysis of water at a semiconductor electrode. *Nature* **1972**, *238*, 37–38.
42. Fujishima, A.; Kobayakawa, K.; Honda, K. Hydrogen production under sunlight with an electrochemical photocell. *J. Electrochem. Soc.* **1975**, *122*, 1487–1489.
43. Wu, X.; Jiang, Z.; Liu, H.; Xin, S.; Hu, X. Photo-catalytic activity of titanium dioxide thin films prepared by micro-plasma oxidation method. *Thin Solid Films* **2003**, *441*, 130–134.

© 2014 by the authors; licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/3.0/>).