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# Microstructures and photocatalytic properties of ZnO films fabricated by Zn electrodeposition and heat treatment

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ABSTRACT

Nanostructured zinc oxide (ZnO) thin films were synthesized via an electrodeposition and subsequent heat treatment method. Using the annealing temperatures ranging from 300 °C to 600 °C, the films develop a variation of microstructures of distinct properties and characteristics. Photocatalytic activities of the ZnO films were studied from photodegradation of methylene blue dye under UV light. Overall, the ZnO films show good photodegradation efficiency and photostabilization. The ZnO film fabricated at 500 °C particularly exhibits relatively high surface area and the strongest photocatalytic activity, which is fairly stable after successive reaction cycles.

## 1. Introduction

Semiconducting oxide photocatalysts, such as zinc oxide (ZnO), titanium dioxide ($TiO_2$), iron oxide ($Fe_2O_3$), and tungsten oxide ($WO_3$), have increasingly received high attentions as the materials offer great potentials to treat organic contaminants in water and air [1–4]. While $TiO_2$ is now being employed relatively widely, ZnO is of increasing interest, owing to its wide band gap similar to $TiO_2$, large exciton binding energy, relatively low cost and non-toxic in nature [5–7]. Many research studies on ZnO photocatalysts have been focusing on developments of ZnO nanoparticles to achieve high surface area and hence more superior photocatalytic activity [8–15]. Their common processing methods include precipitation [16], sol-gel [17], and solvothermal methods [18]. Novel methods utilizing ultrasonic for preparing ZnO nanocomposites have been developed in recent years [19,20].

The typical ZnO powder-based catalysts, however, show tendency to aggregate, are difficult to recover and recycle, hence are relatively expensive for scaling up [21]. A substitute form of ZnO, namely film catalyst comprising of immobilized ZnO particles or layers dispersed on a surface, has thus been developed using methods such as sol-gel [22], chemical bath deposition [23], spray pyrolysis deposition [24], and thermal evaporation [25]. To maintain decent photocatalytic activity, porosity and high surface area are often promoted in these film layers [26–29]. In overall, however, a development of method for effectively tuning the film's structure and analyzing the relationship between microstructure and photocatalytic properties of ZnO films is rather limited.

In this work, an alternative ZnO film synthesizing method that is relatively simple and potentially allows effective modulation of the films' microstructure is proposed and investigated. Particularly, Zn layers are deposited by the electrodeposition technique followed by heat treatment to oxidize the material. The corresponding photodegradation efficiency, reusability and photocorrosion property of the films are analyzed with respect to their microstructure and processing parameters. The understanding gained from the study would provide insights into the fundamentals of ZnO films' photocatalytic properties, and practical processing pathways of the promising ZnO photocatalysts.

## 2. Experimental

### 2.1. Preparation of ZnO thin films

The electrodeposited zinc samples were prepared on polished copper substrates (5 $cm^2$) using an alkaline non-cyanide zincate bath ($Na_2Zn(OH)_4$), consisting of 10 g/L of Zn and 120 g/L of NaOH. The plating was carried out at room temperature (25 °C) with a direct current of 2 A/$dm^2$ for 1 h. Subsequently, the samples were annealed in air using a temperature of 300, 400, 500, and 600 °C for 4 h to transform the plated zinc to zinc oxide.

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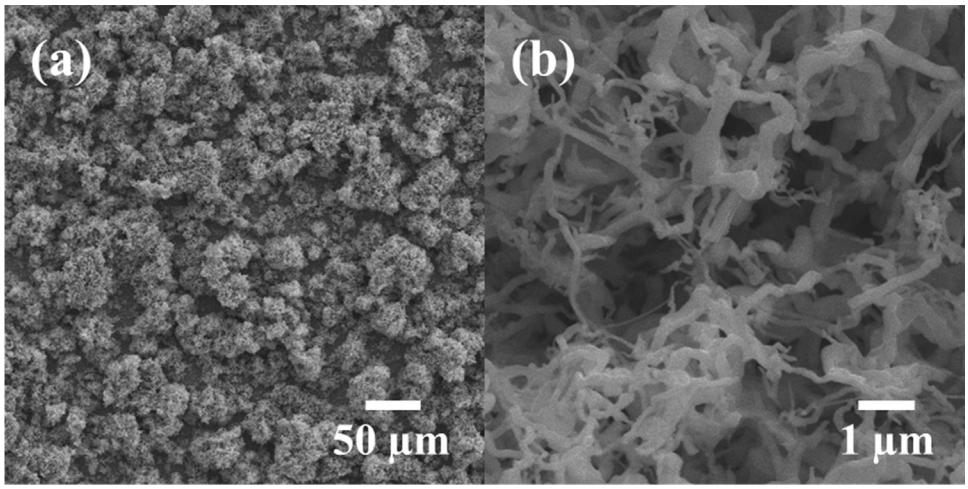


**Fig. 1.** SEM micrographs showing the microstructure of the electrodeposited zinc in different magnifications: (a) low and (b) high.

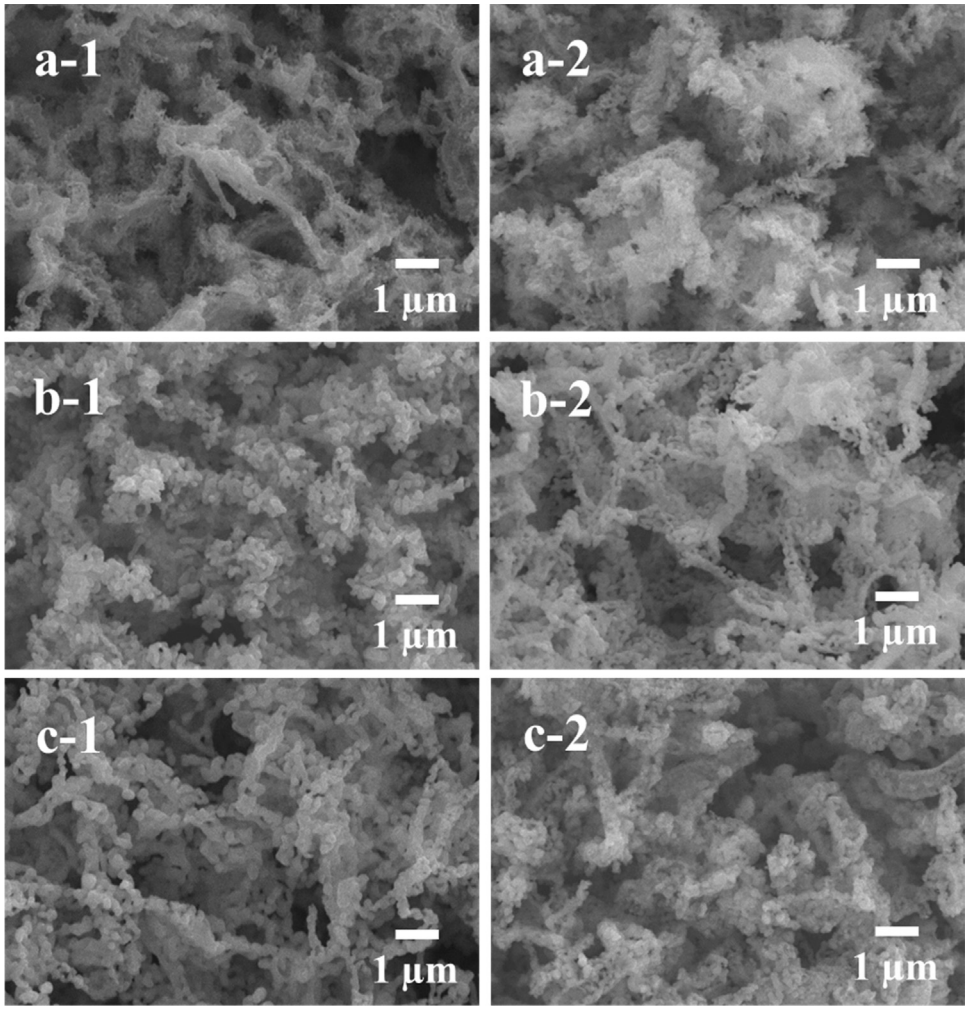


**Fig. 2.** SEM micrographs showing the microstructure of the 3 sets of the ZnO films produced at (a) 400 °C, (b) 500 °C, and (c) 600 °C, before (left) and after (right) the photodegradation tests.

### 2.2. Characterization

The morphology and chemical composition of the samples were then analyzed by scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM/EDX, Hitachi S3400N). X-ray diffractometry (XRD, Philips PW3710) was employed to identify the phase structures. Furthermore, UV–vis diffuse reflectance spectra (UV-DRS) were assessed in a range of 300–4000 nm using a UV–vis spectrophotometer (Hitachi UV-3100) equipped with an integrated sphere attachment.

### 2.3. Photoelectrochemical measurement

Electrochemical impedance measurements were then performed to determine the surface property of the prepared specimens under excitation light generated by a mercury lamp. A saturated calomel electrode (SCE) and a platinum rod were used as reference and working electrodes in a three-electrode cell setup, respectively. The cell was filled with 0.1 M $Na_2SO_4$ electrolyte. The tests were conducted at open-circuit potential (OCP) with a 10 mV amplitude and the frequency