Ceramics International 43 (2017) 8289–8293

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

Temperature-dependent growth of ZnO structures by thermal oxidation of Zn coatings electrodeposited on steel substrates and their photocatalytic activities

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ARTICLE INFO

Keywords:
Zinc oxide
Photocatalytic performance
Surface morphology
Thermal oxidation
Methylene blue

ABSTRACT

In this work, zinc oxide (ZnO) nanostructures were successfully synthesized by thermal oxidation of zinc (Zn) coated steel substrates. Zn coatings were electrodeposited on the mild carbon steel sheet in the sulfate bath by DC current. The zinc coated samples were oxidized in air at distinct annealing temperatures between 400 °C and 800 °C. The phase structure and surface morphology of the ZnO films were analyzed by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The photocatalytic activity of these ZnO layers was examined by means of decomposition of methylene blue (MB) aqueous solutions under UV lamp irradiation for various duration. The findings illustrated that annealing temperatures had a big effect on the morphology and structure of the ZnO layers. The annealed layers showed significantly enhanced photoactivity activity than the pure Zn layer under UV-irradiation. The sample with ZnO nanostructures oxidized at 800 °C exhibited a better photocatalytic degradation of MB than the other samples. This paper can provide an important contribution to the development of efficient photocatalysts for the solution of the environmental pollution problems.

1. Introduction

Zinc oxide (ZnO) nanostructures have been extensively used in various fields including photocatalysis [1], solar cells [2], gas sensors [3], light-emitting diodes [4], hydrogen storage [5], antibacterial agent [6] and photodetector [7] due to their unique optical, catalytic, magnetic and mechanical properties. ZnO in the wurtzite phase and TiO_2 in anatase form are the most utilized transition metal oxides as photocatalysts because of their electronic band gap structure. ZnO is much active in term of the photocatalytic degradation performance than TiO_2, in the most cases owing to its higher quantum efficiency [8–10].

ZnO is crucial n-type semiconductor material with wide band gap (3.37 eV), high exciton binding energy (60 meV) and high electron mobility [11]. ZnO also exhibits a variety of nanostructures, such as nanorod, nanotubes, nanoneedle, nanocomb, nanobelts, nanorings, nanowires, and other complex morphologies [12–14]. ZnO has attracted intensive attention on account of different morphologies and properties for photocatalytic applications [15]. Chemical vapor deposition [16], thermal evaporation [17], hydrothermal processing [18], RF magnetron sputtering [19], sol-gel [20] and metal-organic chemical vapor deposition [21] have been reported for the fabrication of ZnO nanostructures.

In recent years, purity and high-quality ZnO films had been synthesized by thermal oxidation of metallic zinc [22]. Thermal oxidation is a simple and cost-effective method for the production of ZnO nanostructures [23]. The photocatalytic efficiency of ZnO relies on its structural properties such as morphology, particle size, crystallinity and chemical composition. Heat treatments can be used to alter the structural properties [24]. This is the first time to fabricate the ZnO film on the steel substrate by electrodeposition method, and also the formation of the high-efficiency film photocatalysis will provide an attractive opportunity to various industrial application.

Herein, I report a novel, facile and economical route to synthesize ZnO nanostructures on the steel substrates. The samples were prepared by electrodeposition method, followed by annealing in air. The influence of annealing temperature on the structure and surface morphology of these ZnO were discussed in detail. Moreover, the photocatalytic activities of these ZnO nanostructures were investigated by degradation of MB aqueous solution under UV light.

2. Experimental procedure

2.1. Preparation of ZnO nanostructures

Commercial mild carbon steel sheet with a thickness of 1 mm

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http://dx.doi.org/10.1016/j.ceramint.2017.03.162
Received 11 March 2017; Received in revised form 24 March 2017; Accepted 25 March 2017
Available online 27 March 2017

Table 1
Chemical composition of the bath and the parameters of electrodeposition conditions.

Electrolyte composition	Concentration
$ZnSO_4{\cdot}7H_2O$	0.3 M
Na_2SO_4	0.2 M
H_3BO_3	0.2 M
Electrodeposition conditions	
Substrate	Steel
pH	3.2 ± 0.2
Temperature	24 ± 1 °C
Coating time	15 min
Current density	3 A/dm^2
Magnetic stirring	500 rpm

samples were utilized as a substrate in the experiment. Prior to experiment, the samples were cleaned with an aqueous NaOH solution at 60 °C. The samples were then activated in a solution of 20% HCl and rinsed with distilled water. The electroplating process conditions are given in Table 1. The electrolyte was freshly prepared using ultrapure water and analytical grade reagents. The electrolyte pH was adjusted to 3.2 by adding sulphuric acid or sodium hydroxide. The temperature of the electrolyte was kept at 24 ± 1 °C. Electrodeposition was performed using an adjustable direct current (DC) power supply operated in the constant current mode. After the electroplating process, Zn coatings were oxidized at various temperatures ranging from 400 °C to 800 °C for 2 h under air atmosphere so as to achieve ZnO nanostructures on the steel substrate.

2.2. Characterization

XRD (Bruker D2 Phaser) patterns were collected to detect crystalline phase using X-ray diffractometer equipped with a Cu-Kα (λ=1.5406 Å, V=30 kV, I=10 mA) characteristic radiation source in the range of 10–80° with a step size of 2°/min. Scanning electron microscope (SEM, JEOL 6060) were performed to study morphology of prepared samples at an acceleration voltage of 15 kV.

2.3. Photocatalytic performance experiment

Photocatalysis activities were carried out by the decolorization rate of the methylene blue (MB) in aqueous solution using UV light source (Osram, UltraVitalux, 300 W) at ambient temperature. To compare catalyst-free decolorization of MB, a control sample was also prepared. The distance between the light source and the MB solution including immersed catalyst was approximately 200 mm. Then, the solution samples were irradiated with UV light and taken for analysis at regular intervals. Before irradiation, the aqueous solution was kept and stirred in the dark at 1 h to achieve adsorption-desorption equilibrium. There is a direct proportional relation between the absorbance of the solution and its molarity according to Lambert Beer law [25]. Hence, the calibration curve for MB was plotted to convert the absorbance values measured by using a UV–visible spectrophotometer (UV-1240 Shimadzu UV/VIS) to molarity values in Fig. 3. The changes of the main absorbance value of the solutions was measured at 664 nm which corresponds to the maximum absorbance of the MB in the interval time. Time values against molarity values of samples were recorded for certain time. Thus, photocatalytic reaction kinetics of MB and the photocatalytic activities of samples were calculated.

3. Result and discussion

3.1. XRD studies

It is believed that phase and crystallinity of ZnO played a crucial impact on its photocatalytic efficiency. Fig. 1 shows XRD patterns of

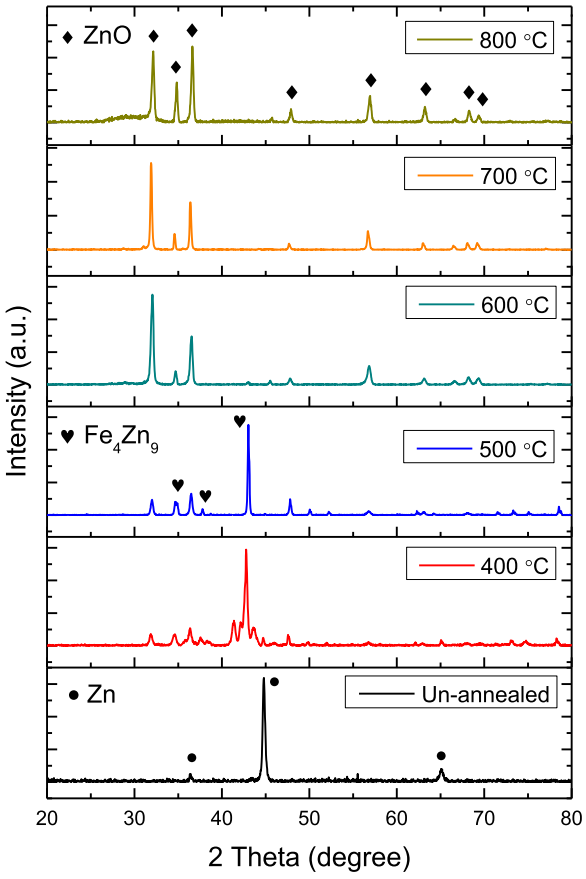

Fig. 1. XRD patterns of the samples for un-annealed and annealed at different temperatures.

electrodeposited pure Zn coating and the ZnO structures annealed at different temperature between 400 and 800 °C. The XRD of the Zn coating without annealing indicated the standard diffraction of the bulk Zn. For the samples annealed at 400 °C and 500 °C, the XRD peaks corresponding to Fe_4Zn_9 were identified in the pattern. When the annealing temperature was increased to 600 °C, the iron-zinc peaks vanished, while ZnO phases were observed. After the Zn layers were annealed at 400–800 °C, the corresponding XRD peaks for (100), (002), (101), (102), (110), (103), (200), (112) and (201) crystal planes confirm the formation of hexagonal ZnO (PDF No: 01-078-4494). It can be seen that the annealing temperatures had obviously profound effect on the crystallinity of the ZnO samples.

3.2. Surface morphology of the ZnO nanostructure

Fig. 2a depicts the surface morphology of pure zinc deposited at 3 A/dm^2. The coating consists of layered hexagonal plates grew in a specific way that relies on the orientation of substrate grains [26]. Fig. 2(b–f) shows effects of thermal oxidation temperatures on the morphology of ZnO nanostructures. As shown in Fig. 2a, Zn layer oxidized at 400 °C started to transform to ZnO and to appear to changes in the surface morphology. It can be observed from Fig. 2c that the 500 °C oxidized ZnO film showed the formation of ZnO nanostructures. According to Fig. 2d, it can be seen that at 600 °C the ZnO layer has a highly dense ZnO nanostructures. When the oxidation temperature increases to 700 °C, the rod like or needle like ZnO nanostructures are observed on the surface morphology (Fig. 2e). At 800 °C, rod like or needle like of ZnO nanostructures are more uniform in shape and size (Fig. 2f). As it can be seen increasing the oxidation temperature, grain size continues to increase.