

## Rapid synthesis of ZnO nano-corncoobs from Nital solution and its application in the photodegradation of methyl orange



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### ARTICLE INFO

#### Article history:

Received 12 August 2014

Received in revised form 18 September 2014

Accepted 13 October 2014

Available online 18 October 2014

#### Keywords:

ZnO  
Photodegradation  
Methyl orange  
Nital solution  
Photocorrosion

### ABSTRACT

This paper reports the synthesis of ZnO with nano-corncoobs morphology; this method consists of two stages of reaction: the first is the formation of ZnO precursor at 70 °C by a mixture formed from a Nital solution (ethanol + nitric acid) and zinc acetate; the second stage occurs at 180 °C, where the combustion process occurs to obtain the ZnO nanoparticles. XRD data showed the presence of hexagonal single-phase ZnO with the wurtzite crystal structure. FE-SEM images indicated that the synthesized ZnO presents nano-corncoobs morphology. The analysis of photoluminescence spectra shows the presence of oxygen vacancies in the synthesized ZnO, which are related to the ratio of polar and non-polar planes. The commercial and synthesized ZnO were used as catalysts for degradation of methyl orange under simulated sun-light. Results showed that synthesized ZnO is more catalytically active for photodegradation under simulated sun-light than commercial ZnO. Photocatalytic activity tests showed that best activity was obtained with uncalcined ZnO powders and this enhanced activity was attributed to the synergistic effect found between the material polar plane and oxygen vacancies. Additionally, electrochemical experiments shown that synthesized ZnO by Nital solution are free of photocorrosion.

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## 1. Introduction

Zinc oxide (ZnO) has a hexagonal wurtzite and cubic zinc blende crystal structure. The wurtzite structure is most stable at room temperature and therefore the most common and intensively investigated for environmental remediation and photovoltaic power production. A great disadvantage of ZnO is the photocorrosion as well as the low photocatalytic efficiency because of its weak visible light absorption and low photocatalytic quantum efficiency, which are caused from fast recombination of photo-generated carriers [1–8].

This is more demanding to expand the application of ZnO as a photo-catalyst to be active in the visible light region. One way is the ZnO doped with different metals, non-metals or with the mixture of other oxides [9–12]. On the other hand, oxygen vacancies play an

important role to expand the visible photocatalytic activity. The atomic arrangements on low index planes of the hexagonal prism on ZnO are stoichiometric, with equal numbers of exposed Zn<sup>2+</sup> or O<sup>2-</sup> ions, while the basal planes and the pyramidal planes are strongly polar, consisting of sheets of Zn<sup>2+</sup> or O<sup>2-</sup>. The polar planes of ZnO play a very important role in solar photocatalytic reactions, because they favor the formation of more oxygen vacancies [13]. Xu et al. reported that visible light absorption capability of ZnO can be enhanced as a result of high concentration of oxygen vacancies. It also helps to produce the H<sub>2</sub>O<sub>2</sub> in photocatalytic processes. Oxygen vacancies can act as trap centers, in addition, oxygen vacancies help in the band gap narrowing as a result of producing an impurity level near the valance band [14,15]. Lv et al. [16] shows that the enhancement of UV activity of ZnO is attributed to the high separation efficiency of photogenerated electron–hole pairs caused by the broadening of the valance band (VB) width induced by surface oxygen vacancies states.

Recently, nanostructures of ZnO have attracted intense attention, since these offer advantages over the bulk ZnO due to their short lateral diffusion length and low reflectivity [17]. Zhang et al.

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[18] have reported the synthesis of TiO<sub>2</sub> nanostructured for the photodegradation of RhB in aqueous solution, and the results showed a higher activity with respect to commercial anatase-TiO<sub>2</sub>.

In this work, the novel and simple Nital-solution and combustion method is used to improve the visible photocatalytic activity of ZnO by combined effect of ZnO nanostructured and increasing oxygen vacancies; the increased activity of ZnO nanostructured has been tested for the degradation of methyl orange under simulated sun-light irradiation.

## 2. Experimental

### 2.1. Synthesis of ZnO nano-corncoobs photocatalyst

The synthesis of ZnO nano-corncob was carried out from Nital solution [19], which is a solution of alcohol and nitric acid; the reaction time of the formation of ZnO nanostructured was about 10 min. The synthesis route was carried out in a typical reflux apparatus as follows: the liquid reaction mixture composed by ethanol (95%) and nitric acid (with 10:1 volume ration) were placed into a round-bottom flask open only at the top; this flask is a triple-neck type and the other two necks were closed with cork lab stoppers. This vessel is connected to a condenser, such that any vapors given off was cooled back to liquid and fall back into the reaction vessel. Then, the vessel was heated at 180 °C for the start of the reaction. When the temperature was 70 °C, then the zinc acetate was incorporated into the flask and this mixture was kept under stirring, heating and refluxing up to 180 °C. The amount of reagents was used to obtain 1 g of ZnO. After reaction time, the flask is completely open and then the powder obtained is maintained at the same temperature to achieve complete evaporation. The powder obtained was divided in three parts and during the degradation experiments these were tested with and without annealing at 400 °C and 600 °C, respectively.

With the finality to know the chemical species present in the reaction mixture, each cork stopper was perforated with a syringe in order to remove or incorporate reactants. The substances extracted were analyzed by infrared spectroscopy from Nicolet 380 FT-IR Spectrometer.

### 2.2. Characterization

The ZnO nano-corncob obtained was characterized by X-ray powder diffraction (XRD) using a Bruker D8 Advance diffractometer with CuK $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). Morphology was determined by scanning electron microscope (SEM) from a JEOL 6490 LV; prior to the analysis, the powder was stuck to carbon tape attached to an aluminum sample holder and then placed into the SEM chamber. The energy band gap ( $E_g$ ) was determined by the Kubelka–Munk function using a UV–vis spectrophotometer (Lambda 35 PerkinElmer Corporation) coupled with an integrating sphere. The room temperature photoluminescence (PL) spectra of ZnO were carried out at Cary Eclipse Fluorescence spectrophotometer (Agilent Technologies) with an excitation wavelength of 370 nm. Specific surface area ( $S_{BET}$ ) was measured by N<sub>2</sub> physisorption through the BET method using Quantachrome NOVA 2000e equipment.

The electrochemical characterization was carried out with a potentiostat/galvanostat AUTOLAB PGSTAT302N connected to a personal computer running the system software (NOVA) for control of experiments and data acquisition. The chemical composition of electrolytic solution was of 1.0 M Na<sub>2</sub>SO<sub>4</sub>. The photocurrents generated were studied by chronoamperometry under simulated sun-light illumination with a solar simulator (Sol1A, Newport).

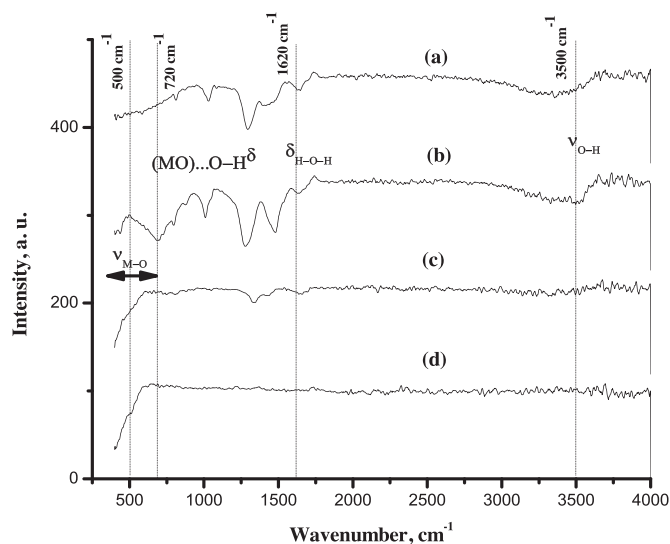
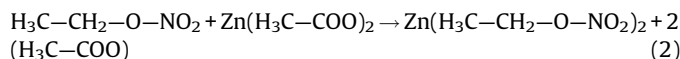
### 2.3. Photocatalytic evaluation

Photocatalytic tests were carried out in a quartz reactor (500 mL). The solution contained 150 mL of methyl orange with concentration of 20 ppm and 150 mg of ZnO catalyst were placed into a quartz reactor under dark condition to reach the adsorption equilibrium. Prior to irradiation, the mixture was placed in ultrasound during 5 min. The photocatalytic reaction was started when the solar-lamp was turn on. Advance of the photocatalytic reaction was followed by means of UV–vis analysis; so, samples were taken at different times during 3 h of reaction. Then the particles of ZnO catalyst were removed by centrifugation at 5000 rpm during 30 min and recovered with a 0.22 mm Millipore GV filter.

## 3. Results and discussion

### 3.1. Synthesis of ZnO nano-corncob

The course of the reaction to the synthesis of ZnO from a Nital solution can be divided in two stages accordingly to the temperature of reaction. The stage 1 and stage 2 were associated with the chemical reactions involved at 70 °C and 180 °C, respectively. During the first stage occurred the condensation reaction between ethanol and nitric acid to produce ethyl nitrate (Eq. (1)). When the zinc acetate is added to the ethyl nitrate solution at 70 °C, it is assumed that a zinc intermediate is formed [20], Zn(H<sub>3</sub>C–CH<sub>2</sub>–O–NO<sub>2</sub>)<sub>2</sub> (Eq. (2)), which quickly decomposes during the combustion reaction at 180 °C to form the ZnO nanoparticles and release of gases like CO<sub>2</sub>, CO, NO<sub>2</sub>, and steam (Eq. (3)) [21].



**Fig. 1.** FT-IR spectra obtained from samples extracted of round-bottom flask with the syringe during the reaction of formation of ZnO. At 70 °C first stage: (a) 5 min, (b) 7 min and at 180 °C second stage: (c) 1 min and (d) 10 min.

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