Journal of Water Process Engineering 12 (2016) 1–7

Contents lists available at ScienceDirect

Journal of Water Process Engineering

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

Template free synthesis, characterization and application of nano ZnO rods for the photocatalytic decolourization of methyl orange

N. Uma Sangari*, B. Jothi, S. Chitra Devi, S. Rajamani

Department of Chemistry, The Standard Fireworks Rajaratnam College for Women, Sivakasi, 626123, India

ARTICLE INFO

Article history:
Received 2 March 2016
Received in revised form 24 May 2016
Accepted 27 May 2016

Keywords:
Ultrasonication
Rods
Aspect ratio
Photocatalytic activity
Photoluminescence

ABSTRACT

Zinc oxide (ZnO) nano rods were synthesized by utrasonication assisted chemical precipitation method without any templates. The influence of pH on the growth of ZnO rods was examined by adjusting the pH of the reaction mixture at values 7, 9 and 13. The as-synthesized rods were characterized by XRD, FT-IR, UV-DRS, SEM and Room Temperature Photoluminescence Spectroscopy. The photocatalytic activity of the synthesized ZnO rods was studied by photocatalytic decolourization of Methyl Orange (MO) dye in presence of UV (365 nm) light irradiation in aqueous solution. The effects of operational parameters such as initial concentration of the MO dye, amount of photocatalyst and initial pH of the dye solution were analyzed. The photocatalytic decolourization of MO dye was confirmed from the decrease in intensity of UV–vis absorption peaks at 464 nm due to lowering concentration of MO dye. Photocatalytic decolourization of MO dye followed pseudo-first order kinetics.

1. Introduction

ZnO, a n-type semiconductor has drawn much attention due to its wide band gap (3.37 eV) and large exciton binding energy (60 meV) at room temperature. It exhibits variety of morphologies. Currently, the synthesis of variousone dimensional ZnO nanostructures such as rods, belts, sheets, rings, wires, prisms, *etc.*, is of focus [1–6]. As an alternative to the TiO_2, it finds application as photoanode in dye- sensitized solar cells. The various other applications of ZnO include photocatalysts, varistors, chemical sensors *etc.* [7–10]. ZnO nano materials are synthesized by different methods such as sol-gel, gel-casting method, thermal evaporation, chemical spray pyrolysis and so on [11–14]. Among all these methods, sonochemical precipitation has become a new trend in the field of materials science due to its capability to produce products with high crystallinity and purity [15,16].

Photocatalysis is an important property of semiconductors. ZnO, as it is non-toxic and less expensive plays a vital role in the photocatalysis for the remediation of various pollutants such as dyes, organics and metal ions [17–19]. In general, when the semiconductors are irradiated with the light having energy higher than their band gap, electrons from the valence band are excited to conduction band and an equal number of holes are produced in the valence band. Some of these photogenerated holes and electrons move to the semiconductor surface and they undergo redox reactions with suitable substrates. The trapped holes react with chemisorbed water or surface hydroxyl species to produce OH° free radicals and the electrons reduce the oxygen molecules to superoxide anions $O_2^{-\bullet}$ which lead to produce $OH^{\bullet}$ free radicals. These free radicals are responsible for the photooxidation of the pollutants that are adsorbed onto the surface of the semiconductor.

The main objective of this work is to optimize the pH of the precursor medium to prepare ZnO nano rods at room temperature and to explore the photocatalytic decolourization of acidic dye methyl orange (MO) rods using UV light source (365 nm). Methyl orange is an important mono azo dye used in dyeing and printing textiles [20]. It is also used mostly as a colorant and an acid-base indicator [21]. Azo dyes are known to be highly susceptible for biodegradation and hence we have chosen it as the model pollutant [22]. The effect of various operational parameters such as the dose of the catalysts, initial concentration of the methyl orange dye, initial pH of the dye solution and UV light irradiation time were optimized for the efficient decolourization of MO dye. We have adopted sonochemical precipitation method using Zinc nitrate and a strong base Potassium hydroxide as precursors. The products were characterized by XRD, SEM, FT-IR, UV-DRS and Photoluminescence Spectroscopy.

* Corresponding author.
E-mail address: umasangariselvakumar@gmail.com (N.U. Sangari).

http://dx.doi.org/10.1016/j.jwpe.2016.05.011
2214-7144/

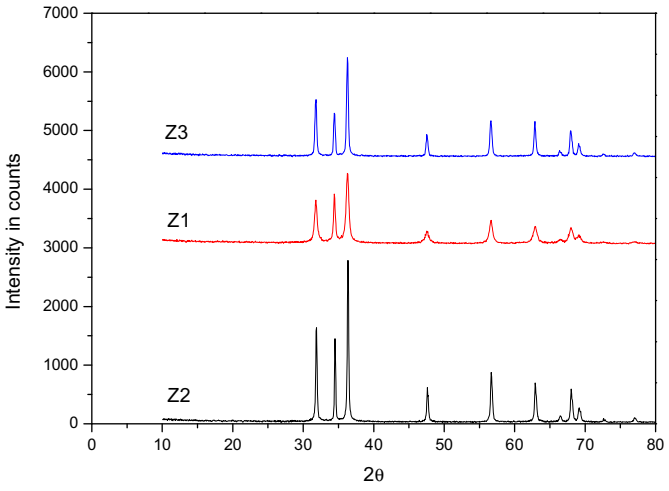

Fig. 1. XRD patterns of ZnO synthesized at different pHs. (a) pH 9 (Z2), (b) pH 13 (Z1) and (c) pH 7 (Z3).

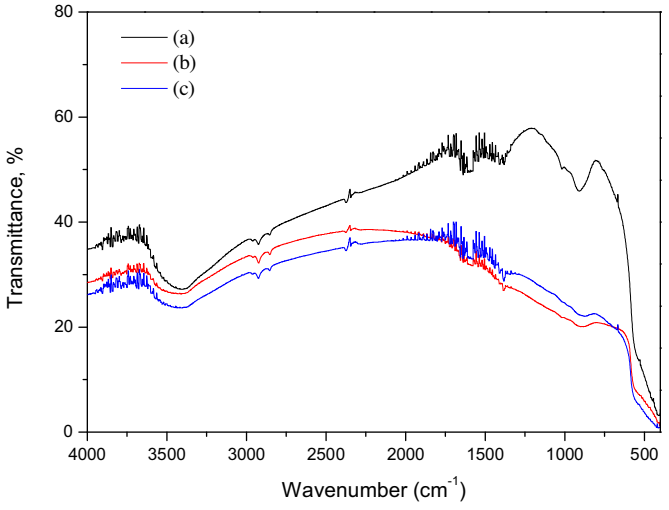

Fig. 2. FT-IR spectra of nano ZnO rods synthesized at (a) pH 13 (Z1), (b) pH 9 (Z2) and (c) pH 7 (Z3).

2. Experiment

2.1. Materials

The chemicals, Zn $(NO_3)_2$ (99% purity, Merck), KOH (85% purity, Merck) and methyl orange dye (Merck) were procured and used without further purification.

2.2. Synthesis of ZnO nano rods

In brief, the synthesis procedure is as follows: 1 M KOH solution was added drop wise very slowly into the Zinc nitrate solution with constant stirring till the required pH of either 13, 9 or 7 was attained. During stirring, a milky white suspension of Zn $(OH)_2$ was obtained. The above solution was sonicated for 30 min in an ultrasonicator (Power: 25 KW). The resultant solution was kept overnight at room temperature. The formed precipitate was irradiated with Microwaves at 180 W for 30 min (Samsung MW 73 V), filtered and washed thoroughly with double distilled water for several times. After this, the resultant precipitates were filtered and calcined at 200° C in a vacuum oven for two hours. The products obtained from three different precursor solutions of pH 13, 9 and 7 are labeled as Z1, Z2 and Z3 respectively.

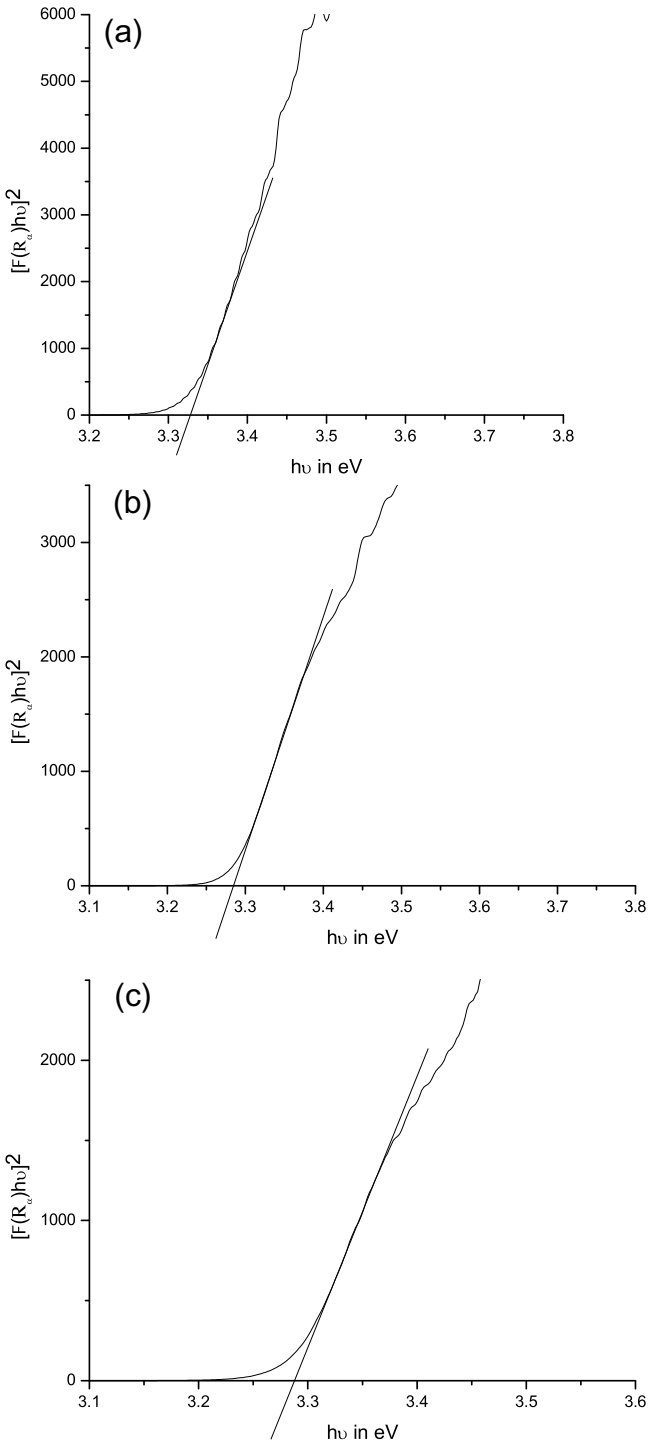

Fig. 3. Plot of $[F(R\alpha)h\gamma]^2$ against $h\gamma$ in eV for ZnO nano rods synthesized at (a) pH 13 (Z1), (b) pH 9 (Z2) and (c) pH 7 (Z3).

2.3. Evaluation of photocatalytic activity

The photocatalytic decolourization of 15 ppm MO dye solution was carried out in presence of 8 W low pressure mercury vapor lamp excited at 365 nm. Exactly, 0.8 g L^{-1} of the synthesized ZnO catalyst was suspended in 50 mL of MO dye solution and stirred thoroughly for 30 min in dark to achieve adsorption- desorption