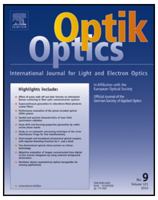
Optik 154 (2018) 303–314

Contents lists available at ScienceDirect

Optik

journal homepage: www.elsevier.de/ijleo



Full length article

Observation of high photocatalytic activity by tuning of defects in chemically synthesized ethylene glycol capped ZnO nanorods

Partha Kumbhakar, Subrata Biswas, Pathik Kumbhakar*

Nanoscience Laboratory, Department of Physics, National Institute of Technology Durgapur, 713209, West Bengal, India

ARTICLE INFO

Article history:
Received 4 July 2017
Accepted 8 October 2017

Keywords:
Optical properties
Photo-catalytic
Photoluminescence
ZnO
Defect tuning
Thermal annealing
Chemical synthesis
Nanorod

ABSTRACT

In this work, we have reported the tuning of defects by simple thermal annealing of as-synthesized ethylene glycol capped ZnO nanorods at 200–600 °C temperatures. X-ray diffraction (XRD) data has confirmed the formation of Wurtzite structure of ZnO and the presence of a small amount of tensile strain is confirmed by Williamson – Hall analyses of XRD data. The lattice strain is found to increase with increasing temperature up-to 400 °C and on further increase in temperature it is decreased. To study the influence of defects on photo-catalytic properties of the samples, the degradation of a test dye, namely Methylene Blue (MB) under UV–vis light irradiation has been carried out and the reaction kinetics has been determined by Langmuir-Hinshelwood model. It has been found that 400 °C annealed sample exhibits the highest photo-catalytic dye degradation efficiency of ~83%, within only 20 min. The effect of initial MB dye loading on photo-catalytic efficiency of 400 °C annealed sample has also been tested and reported an optimum value of dye concentration. The successful introduction of defect states in 400 °C annealed sample, as confirmed by PL measurement, has played an important role to achieve the high photo-catalytic activity in the samples.

1. Introduction

The uses of hazardous dyes in textile industry have been a ubiquitous problem of human civilization and efforts are required to counter its effect on environment. The use of semiconductor photo-catalyst for the degradation of dye molecules dissolved in water is an age-old technique [1–3]. When a photo-catalyst is illuminated with the light of appropriate wavelength, electron–hole pairs diffuse out to the surface of the photocatalyst and participate in the photochemical reaction. Those free electrons and holes transform the surrounding oxygen or water molecules into $OH^{\bullet}$ radicals having strong oxidizing ability. These radicals are responsible for the effective decomposition of harmful organic dyes into its less hazardous simpler forms. Among different kinds of semiconductors and its composites nanomaterial of TiO_2, ZnO, ZnS, CdS, WO_3 etc. have been considered extensively due to their useful properties [3,4]. TiO_2 is the most commonly used effective photo-catalyst. However, recently it has been found that ZnO with a wide band gap of ~3.2 eV is a good and an alternative semiconductor material for its high efficiency, photochemical stability, non-toxic nature and low cost preparation technique [5]. It has been

---

* Corresponding author.
E-mail addresses: pathik.kumbhakar@phy.nitdgp.ac.in, nitdgpkumbhakar@yahoo.com (P. Kumbhakar).

https://doi.org/10.1016/j.ijleo.2017.10.039

reported earlier that due to lower exciton recombination rate and greater surface area ZnO has showed promise to achieve a high photo-catalytic efficiency [6].

Several researchers in the past have also reported the benefits of using a smaller sized nanostructure with various microstructures for the degradation of organic dyes [7–9]. They have demonstrated that a larger surface to volume ratio and use of some specific shapes of ZnO elevates the rate and efficiency of dye adsorption at active sites and thus dye degradation rate is improved [7]. Different methods have been tried by earlier researchers to enhance the photocatalytic activity of ZnO by tailoring its size, facets, and surface area [7–9]. Recently, Jang et al. have reported the relationship between the crystal growth plane of ZnO nanocrystals and their photocatalytic efficiency [8]. They have found that the availability of greater proportion of polar surfaces (*001*) led to a greater photocatalytic activity [8]. They reported that $OH^{\bullet}$ ions prefer to adsorb onto polar (*001*)-Zn surface due to its positive charge, which can react with hole (h^+) to generate $OH^{\bullet}$ radicals and thus enhances the photo-catalytic activity of the sample. The e^-/h^+ pair is the key factor in determining the photocatalytic reaction rate.

Amongst other techniques, thermal annealing is a simple technique as it may effect on the electron-hole recombination rate in ZnO nanostructure and thus photocatalytic dye degradation efficiency of the photo-catalyst may be tailored [8–12]. The effect of annealing and aspect ratio of ZnO and TiO_2 nanostructures on photo-degradation of MB dye has been dealt with previously by several researchers [8–12]. Lv et al. reported that ZnO shows 88% degradation of dye in 180 min due to annealing at 800 °C [11] as compared to 73% for annealed sample at 400 °C. Yu et al. has reported that TiO_2 shows good photo-catalytic activity at 700 °C [9] compared to room temperature sample. In all above reports we have observed that the annealing temperature is quite high to obtain a reasonable photo-catalytic performance. Besides the aspect ratio, shape and size, the presences of surface defects on ZnO are another very important factor for prompting its photo-catalytic performance. In fact, the defects on ZnO have been extensively characterized by various techniques, and their roles in adsorption and surface reactivity have been considered and shows that different oxygen defects (oxygen vacancies and interstitial oxygen) and zinc defects (zinc interstitial) that formed in a solvothermal process has an impact on the photo-catalytic activity of ZnO [10]. Zinc interstitials and oxygen vacancy both play very important roles in photo-catalytic activity [10].

However, in this work we have reported the synthesis of ZnO nanorod by solvothermal technique and then we have demonstrated the tuning of surface defects by simple thermal annealing the as-synthesized sample at 200°, 400° and 600 °C temperatures and we could achieve high photo-catalytic degradation efficiency. FESEM, TEM and XRD techniques have been used to obtain the microstructure and phase of the samples. Optical absorption and photoluminescence (PL) emission spectroscopies have been used to confirm the band gap and the presence of defects in the samples. Photo-catalytic property of all the samples have been investigated and found that the sample which has been annealed at 400 °C showing the highest MB dye degradation efficiency of 83%. The Langmuir–Hinshelwood (L-H) model has been used to evaluate the kinetics of dye degradation. The optimized degradation efficiency for different dye concentration has been evaluated and is found to be highest for MB-dye of concentration 20 mg/L. The effect of particle shape and defect states on kinetics of photo-catalytic degradation has been investigated. A generalized mechanism of chemical reaction of MB dye on photocatalysis has also been reported in this work.

2. Experimental

2.1. Synthesis of samples

We have synthesized the ZnO nanorods with varying aspect ratio in two steps. At first ZnO nanoparticles have been freshly synthesized by solvothermal route and then the as-synthesized samples have been isochronally annealed for 2 h at various temperatures within the temperature range of 200–600 °C. For the synthesis of ZnO nanoparticle by solvothermal technique, 0.016 M of Zinc acetate dehydrate $[Zn\,(CH_3COO)_2]\,2H_2O$ is dissolved in 40 ml of EG under vigorous stirring for 90 min. Then the solution is transferred into a Teflon-lined autoclave maintained at 160 °C for 8 h. Then the autoclave is left for cooling at room temperature and the precipitate is collected by centrifugation and washed several times with DI water. The precipitate is then dried in our laboratory oven at 100 °C for 2 h to obtain the final ZnO powder. The obtained sample is divided into four parts, one part is annealed in air ambient at 200 °C denoted hereby as S#200, another part at 400 °C denoted as S#400, another at 600 °C denoted as S#600 and the fourth part is as-synthesized sample denoted as S#RT. All the samples are further characterized for determining their nanostructures and measurement of their optical properties.

2.2. Characterization

The XRD patterns have been recorded using a PAN Analytical X-Pert Pro Diffractometer using *Cu Kα* radiation in the scan range 20–65°. The formations of ZnO nanorod have been confirmed by using TEM and FESEM. TEM images have been recorded in a TEM (JEOL JEM 2100) after dispersing the samples in a carbon coated copper grid. FESEM (ZEISS SIGMA) has been used for structural analysis. The optical absorption spectra of all the samples have been recorded after dispersion in de ionized (DI) water using an UV–vis spectrophotometer (HITACHI U-3010). The PL spectra have been measured at RT by using a PL spectrofluorometer (Perkin Elmer LS 55) by keeping them in a four side polished cuvette of path length 1 cm.