



Solution grown ZnO rods: Synthesis, characterization and defect mediated photocatalytic activity



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ABSTRACT

The aqueous solution growth process of ZnO rods, starting from zinc hydroxide formed during the ultrasonic precipitation of zinc acetate and ammonium hydroxide has been demonstrated here. A dispersion consisting of 0.3 (w/v) % zinc hydroxide in water on heating at $80 \pm 5^\circ\text{C}$ for 6 h has resulted in the formation of ZnO rods having an aspect ratio between 8 and 12. We have monitored the growth of ZnO rods as a function of different reaction parameters. The as-prepared rods have also been characterized by optical and Raman spectroscopic methods in addition to other techniques. Further, we also investigated the photocatalytic degradation of methyl violet, which is a well known textile pollutant by using the as-prepared ZnO rods and found that the degradation was more effective using a 365 nm light source than using a 254 nm light source. This result confirms that the as-processed ZnO rods could be used directly under sunlight for the degradation of methyl violet present in polluted water. Our experimental results, confirmed that the sample with more oxygen defects shows better photocatalytic degradation of the dye molecule due to the involvement of oxygen vacancy defects and oxygen interstitials in the charge recombination process and helps in better catalytic reaction under a UV lamp.

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1. Introduction

Zinc oxide (ZnO) has currently drawn intense global attention due to its projected application as an alternative photoanode to TiO_2 in Dye-Sensitized Solar cells [1,2]. Other major applications of nanostructured ZnO are as photocatalysts, sensors, and also as light emitting diodes [3]. Various attempts have been carried out in controlling the size and shape of ZnO nanocrystals, as it provides a better mode for investigating the dependence of electronic and optical properties on the size confinement and dimensionality. The large number of publications appearing in the area of ZnO based DSSCs, throw light on the increased use of ZnO and ZnO based nanomaterials as alternative photoanodes to TiO_2 in the Dye-Sensitized Solar cells [4–6]. In addition, the recent studies indicated that ZnO

can also be used as a promising photocatalyst for the degradation of organic pollutants under UV/visible/solar irradiation [7–13]. Most of the photocatalytic or photodegradation studies using ZnO as a catalyst have been focussed on rhodamine B, methylene blue or methyl orange dyes, with a very few on methyl violet [14,15]. However, the important point to note is that in both the cases, the applications of ZnO are strictly dependent on its morphology, dimensionality, size, shape and surface defects [16].

Among the various multifarious synthesis techniques available for the preparation of ZnO nanostructures [3–6], sonochemical process [17,18] turned out to be a promising option due to its capability to control the purity, crystallinity and composition of the desired product, in addition to its cost effectiveness [18–22]. The available reports strongly suggested that careful control of synthetic parameters and growth conditions can result in ZnO nanostructures with exotic size, shape and morphology by the sonochemical process. In most of the cases, formation of ZnO occurred via the intermediate formation of $\text{Zn}(\text{OH})_2$ and $[\text{Zn}(\text{OH})_4]^{2-}$ [23,24]. In spite of the large number of information available on the growth of ZnO in various forms, there is still considerable uncertainty regarding the possible role of zinc hydroxide, its concentration, the mechanism by which

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zinc hydroxide converts to zinc oxide and the factors governing the product morphology. Our main objective was to optimize the reaction conditions to prepare ZnO rods at low temperature and correlate its formation with reaction parameters such as temperature, duration and concentration of the starting zinc hydroxide precursor. For this purpose, we have used sonication assisted chemical precipitation process using a weak base like NH_4OH to prepare zinc hydroxide. As a part of our on-going program on DSSC, we prepared ZnO flower, cubes and rods by both precipitation and sonochemical techniques and studied their performance as photoanodes in DSSC [25–28]. Further, we have also investigated the photocatalytic application of the synthesized materials for environmental applications. In here, we report the detailed growth process of ZnO rods and the photocatalytic degradation of a cationic dye methyl violet using the solution grown ZnO rods. The methyl violet (MV) is a typical example of industrially pertinent toxic cationic dye having a lot of detrimental effects on global lives. It is largely used as a purple dye in textile, leather, paint, in paper industries as tinter to give a visually bright appearance in paper, and testing pH ranges as an acid–base indicator [14,15,29–31]. Most of the reported photocatalytic studies of ZnO are on methylene blue and methyl orange by using UV light of 254 nm radiation. There are hardly any reports on the degradation of methyl violet dye using ZnO nanorods [14,15]. It is interesting to note that the UVC component of sunlight with wavelengths between 100 and 280 nm, is very energetic but is filtered out by the ozone layer, and never reaches earth whereas the UVA is long range radiation between 320 and 400 nm which is not readily absorbed by the ozone layer and 95% of it gets through and reach the earth's surface. Therefore, in this work we have investigated the photocatalytic degradation of methyl violet by solution processed ZnO rods using both two different wavelengths of UV lights such as 254 and 365 nm, respectively.

2. Experimental

2.1. Synthesis of ZnO

ZnO rods have been prepared from Zinc acetate dihydrate ($\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, 99.5%AR, Merck Ltd. Germany) as zinc source and ammonium hydroxide (30% GR, Merck Ltd. Mumbai, India) as a precipitating agent. Acetone (Merck Ltd. Germany) and ethanol (Merck Ltd. Germany) were used as washing liquid and dispersion medium, respectively, without further purification. All the reactions have been carried out in aqueous media using distilled water as a solvent.

Initially, precipitation was carried out using 0.1 M zinc acetate dihydrate solution and ammonium hydroxide as the precipitating agent under sonication (Ultrasonic power 250 W, ultrasonic frequency 25 kHz, probe diameter, 25 mm). A homogeneous white precipitate of zinc hydroxide was formed by the drop-wise addition of NH_4OH during sonication (2 h) until the pH of the zinc acetate solution was raised to 9.0 ± 0.5 . Subsequently, the precipitate thus formed was centrifuged and dispersed in distilled water followed by heating at $80 \pm 5^\circ\text{C}$ for several hours on a magnetic stirrer with constant stirring to induce the nucleation and growth of zinc oxide. In order to elucidate and understand the conversion of precipitated zinc hydroxide to zinc oxide, we have varied the reaction durations and the precursor concentrations. In all the cases the reaction temperature was maintained at $80 \pm 5^\circ\text{C}$. The obtained products were further centrifuged at $\sim 12,000$ rpm and washed with distilled water and acetone followed by drying under an IR lamp. To investigate the effect of reaction duration on the nucleation and formation of ZnO from zinc hydroxide, an aqueous solution growth process was carried out by taking a 0.3 (w/v) % concentration of zinc hydroxide precursor solution in distilled water and heating the mixture at $80 \pm 5^\circ\text{C}$ for 2, 4 and

6 h, respectively, on a magnetic stirrer. Throughout the growth process, pH of the precursor solution was monitored very carefully. While the initial dispersion of zinc hydroxide in distilled water at room temperature shows a pH of 7 ± 0.5 , but with an increase in temperature to $80 \pm 5^\circ\text{C}$, the solution becomes alkaline with a pH of 8 ± 0.5 due to more ionization at elevated temperatures. This high pH of the growth solution persists for 2–4 h and beyond which it decreases to 6 ± 0.5 after 6 h. The corresponding samples formed were denoted as S-1, S-2 and S-3, respectively, for convenience. In order to investigate the effect of concentration of the precursor at a fixed reaction duration of 6 h, the growth process has been repeated with a dilute (0.16 (w/v) %) concentration of the precursor hydroxide. It was observed that the final pH of both the precursor growth solution was around 6.0 ± 0.5 . The corresponding sample formed is denoted as S-4 in rest of the manuscript.

2.2. Characterization

The dried powder was characterized by powder X-ray diffraction (XRD) analysis on a X'pert pro MPD XRD of PAN analytical with $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). In order to understand the thermal decomposition nature of the samples, thermo gravimetric analysis (TGA) and differential scanning calorimetric (DSC) studies were carried out on the powder samples from room temperature to $\sim 1000^\circ\text{C}$ at a heating rate of $10^\circ\text{C}/\text{min}$ on a NETZSCH 449C simultaneous thermal analyzer. In order to monitor the consequent changes in the morphology that may have appeared during the reaction, Scanning Electron Microscope (SEM) and Field Emission Scanning Electron Microscope (FESEM) studies were carried out on a LEO 430i (Carl Zeiss) Scanning Electron Microscope and Supra 35 VP (Carl Zeiss) Field-Emission Scanning Electron Microscope, respectively. The particle morphology and local crystallographic structure were studied by Transmission Electron Microscopy (TEM) and High-Resolution Transmission Electron Microscopy (HRTEM), respectively, on a Tecnai G2 30ST (FEI) high resolution transmission electron microscope operating at 300 kV. Fourier transform infrared (FTIR) spectra of the samples were recorded on a Nicolet 380 FTIR spectrometer using KBr. BET surface area of the samples were measured by nitrogen sorption isotherm process using Quantachrome twin surface area analyzer (NOVA 4000e). The absorption spectra were measured on a UV–Vis–NIR Spectrophotometer (Shimadzu UV-3600). The optical properties of the ZnO rods were further evaluated by recording the room temperature photoluminescence spectrum (PL) on a Steady State Spectrofluorometer (QM-40, Photon Technology International, PTI) using a 150 W Xenon lamp as an excitation source, at an excitation wavelength of 345 nm and a band pass of 5 nm. Raman Spectra were obtained using a Renishaw in via Reflex micro Raman spectrometer with an argon ion (514.6 nm) laser. The spectra were collected with a resolution of 1 cm^{-1} . The X band Electron paramagnetic resonance measurements of the powder samples were performed using a Bruker EMX spectrometer at room temperature and the microwave frequency was measured with a Hewlett-Packard 5246 L electronic counter. About 5 mg of each sample was taken in a quartz tube of 1 mm diameter. Instrumental parameters used for the measurement are frequency = 9.45 GHz, BO-field = 346 mT, BO-sweep = 200 mT, mod amplitude = 0.2 mT, and sweep time = 60 s.

2.3. Photocatalytic activity studies

After thorough characterization and property evaluation, the photocatalytic activity of few selected ZnO samples were studied by monitoring the photocatalytic degradation of 10^{-5} M methyl violet (MV) solution in presence of an 8W UV lamp (UVLS-28 EL Series) having an average light intensity of $0.6 \text{ mW}/\text{cm}^2$, excited at 365 nm (3.39 eV) and 254 nm (4.88 eV), respectively, using a very simple

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