



Wet chemically synthesized catalytic nanorods for the deactivation of thymol blue and their statistical analytical applications

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Received 15 September 2014; received in revised form 8 November 2014; accepted 9 November 2014

Abstract

Needle-shaped zinc oxide nanorods (ZnO-NRs) were obtained from zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) and sodium hydroxide (NaOH) via a low-temperature ($\sim 90^\circ\text{C}$) wet chemical solution process with a short reflux time. The NRs were characterized in terms of their morphology, crystallinity and optical properties using standard characterization techniques such as X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) and UV–visible spectroscopy. The grown NRs were shown to degrade organic thymol blue (TB) dye with enhanced photocatalytic efficiency ($\sim 77.27\%$). The effective concentrations of ZnO-NRs were determined, optimized and validated via standard analytical techniques. For the quantitative and qualitative analysis of ZnO-NRs, statistical analytical parameters were applied to provide necessary information for the proposed method, such as solution stability, selection of wavelength, specificity, precision, accuracy, working range, limit of detection (LOD) and limit of quantitation (LOQ) at a very low concentration level of the photocatalyzed solution. The UV–visible absorption spectra of the photocatalyzed solutions were evaluated.

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Keywords: Chemical synthesis; Photocatalytic activity; Needle-shaped nanorods; Thymol blue

1. Introduction

Metal oxide nanomaterials are considered to be potential candidates to play important roles in the environment due to their unique functional properties, such as large surface areas, high reactivities, high photosensitivities, good absorption capacities, enhanced quantum efficiencies, non-toxic natures and wide band-gaps, which have resulted in metal oxide nanomaterials receiving considerable attention in various fields [1–5]. Several types of nanostructures such as SnO_2 , TiO_2 , and Fe_2O_3 ; doped materials ($\text{Cu}_2\text{O}/\text{ZnO}$, iron-doped ZnO, Fe–ZnO, Ni-doped, and Mn-doped); and other transition metal oxides (TMOs) are used in solar cells, optical coatings, corrosion protection, semiconductor thin film devices, and so on. These materials have been produced using several growth techniques, and their properties have been reported [1–5]. Gold

nanoparticles and zinc oxide nanorods were co-sputtered to form nanocomposites (NCs) under different annealing conditions [6]. Recently, Mishra et al. [7] reported the growth of different metal oxide nano-microstructures and their interconnected 3D networks using an FTS approach and reported the growth mechanism in detail [7]. The continued growth of numerous types of nanomaterials, including metals, metal oxides, composites, quantum dots, and carbon nanotubes, is in demand for current and future applications and has the potential to greatly impact safe bio-environments [8–10]. Among various types of metal and metal oxide nanomaterials, ZnO exhibits especially unique and fascinating properties (electrical, optical and mechanical); it absorbs a larger fraction of solar energy and has high catalytic efficiency, a nontoxic nature, high photosensitivity, high stability, and a high band gap (3.37 eV) with a large exciton binding energy (60 MeV) [11–14]. ZnO exhibits various types of nanostructures that are produced via different synthetic processes. As a result, ZnO is known as a family of nanostructures that includes nanowires,

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nanoparticles, nanobelts, nanobridges, nanonails, whiskers, nanoribbons, nanorods, nanotubes, nanospheres and nano-flowers [15–23]. Concerning photocatalytic properties, Jin et al. [24,25] reported a novel concept for sensitive photoluminescence tetrapod-like ZnO nanostructures. Several applications in various fields have been reported for ZnO nanostructures, such as solar cells, chemical, biological, gas and UV sensors [26], piezoelectric devices, light emitting diodes, sunscreen, cosmetic, antibacterial, antifungal and antimicrobial materials, bio-imaging, disease diagnosis and cancer treatment [27–33]. The nano- and microstructures of ZnO also have the capability to imitate filopodia cells and can target HSV-1 in pathogenesis [34]. The tetrapod-like structures of ZnO have the ability to block the entry and spread of the HSV-2 virus into target cells and can neutralize HSV-2 virions [35]. In another report, the cellular mechanism of dissolved Zn^{2+} ions was investigated in presence of tetrapod-like ZnO structures [36]. Various methods have been employed for the synthesis of zinc oxide nanostructures including chemical vapor deposition (CVD), vapor–liquid–solid synthesis [37], flame transport synthesis [38], spray pyrolysis, ion beam-assisted deposition, laser-ablation, sputter deposition and template assisted growth [39,40]. The ZnO nanomaterials are highly versatile photocatalyst materials that affect various dyes; they have been shown to degrade methyl green (MG), methylene blue (MB), rhodamine B (RhB), etc. and are highly effective under intensity of UV–visible light [41–44]. These dyes and their related organic compounds are carcinogenic and cause bio-environmental and health problems in the environment. Therefore, the degradation/deactivation of dyes into smaller molecules is currently a pressing issue in the control of organic pollutants in the environment. Various physical, chemical and biological methods such as coagulation, flocculation, activated carbon adsorption and reverse osmosis have been employed to control organic environmental pollutants. Among the methods frequently used to degrade organic dyes, photodegradation, which generates free radicals and isolates the degraded molecules or species from the organic compounds, is one of the most promising deactivation processes. Several techniques such as inductively coupled plasma atomic emission spectrometry (ICPAES), photoluminescence (PL), atomic absorption spectrophotometry (AAS), energy-dispersive X-ray spectroscopy (EDX) and fluorescence, liquid chromatography electrospray ionization ion trap mass spectrometry (LC–IT–MS), HPLC and ion-pairing high-performance liquid chromatography mass spectrometry (IP–HPLC–MS) have been employed for electron quenching and photocatalytic degradation [44].

In this paper, needle-shaped ZnO nanorods (ZnO-NRs) were successfully synthesized via a low-temperature ($\sim 90^\circ\text{C}$) soft chemical solution process and characterized via sophisticated techniques such as XRD, FESEM and UV–visible spectroscopy. Based on the synthesis and characterization, the possible growth mechanism of the ZnO nanoneedles was described. The analytical measurements were performed to determine the effective concentration of ZnO-NRs in a photocatalyzed suspension solution. The photocatalytic activity of the ZnO-NRs for the photodegradation

process was examined by UV–visible spectroscopy. The effect of ZnO-NR concentration on the degradation of TB dye was determined and validated using statistical analytical parameters based on the International Conference on Harmonization (ICH) for standardization of analytical procedures.

2. Materials and methods

2.1. Experimental

2.1.1. Wet chemically synthesized zinc oxide nanorods (ZnO-NRs) and their characterization

Needle-shaped ZnO-NRs were successfully synthesized from zinc acetate dihydrate ($\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$) and sodium hydroxide (NaOH) via a wet chemical process. All of the chemicals for the synthesis of ZnO-NRs were purchased from Aldrich Chemical Co. Ltd. and used without further purification. In a typical experiment, zinc acetate dihydrate (0.3 M) was first dissolved in doubly deionized distilled water (DDDWW) and stirred for 30 min to completely dissolve the zinc salt. To this mixture, strong alkali sodium hydroxide (NaOH, 1 M) was added gradually until the pH reached 12.0. A viscous, white-colored suspension appeared in the beaker for few seconds and then disappeared after some time. The white-colored solution was transferred to a two-necked refluxing pot and refluxed at 90°C in 1 h. Although no stable precipitate was observed initially in the refluxing pot, an excess of white precipitate settled at the bottom of the pot as the refluxing time increased. After reaction completion, the refluxing pot was cooled at room temperature. The obtained white precipitate was sequentially washed several times with methanol (MeOH), ethanol (EtOH) and acetone and dried in glass petri dishes at room temperature. A schematic flow chart for the synthesis of needle-shaped ZnO-NRs is shown in Fig. 1. Finally, the morphology, crystallinity and optical properties of the obtained white powder were characterized.

Morphological characterizations were performed using FESEM, while crystallinity was analyzed by XRD with $\text{Cu}_{K\alpha}$ radiation ($\lambda = 1.54178 \text{ \AA}$) in the range of $20\text{--}65^\circ$ at a scan speed of 6° min^{-1} . For FESEM observation, the nanopowder was sprayed on carbon tape and sputtered with osmium tetroxide (OsO_4) for 5 s. The nanostructured powder was placed in the sample holder and analyzed at room temperature.

2.2. Photocatalytic activity of synthesized ZnO-NRs

The photocatalytic degradation of TB dye in presence of ZnO-NRs was carried out in a photocatalytic glass reactor as previously described [13, 14]. For photocatalytic evaluation, approximately 5 mg of ZnO-NRs was added to $1 \times 10^{-5} \text{ M}$ of TB dye solution in 100 mL of distilled water under continuous stirring. A blank experiment was also performed to confirm that no reaction takes place in absence of UV-light. A 5 mL sample of ZnO-NRs with TB dye was extracted at each testing point, and the catalyst was separated completely by ultracentrifugation before taking UV–visible readings. The UV-light was irradiated on the photocatalytic

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