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A new, cost-effective solar photoactive system N-ZnO@polyester fabric for degradation of recalcitrant compound in a continuous flow reactor

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ABSTRACT

A novel solar photoactive system, consisting of N-ZnO particles coated on a polyester fabric (PF), is prepared using a simple heat attachment method. The photocatalytic activity of the photoactive system (N-ZnO@PF) for amaranth (AM) degradation is studied in a circulation thin-film fixed-bed reactor (TFFBR) under solar light. The presence of N-ZnO particles evenly coated on the PF surface is verified by XRD, ATR-FTIR, and SEM analyses. On the basis of DRS analysis, N-ZnO@PF is shown to have remarkable visible-NIR absorbance. N doping, which is confirmed by XPS and NEXAFS analyses, is responsible for a remarkable spectral response. As initial AM concentration, flow rate, reactor inclination, and salinity increases, the AM degradation decreases. AM degradation reaches to 99.2% at 10 mg/L concentration. The IUPAC figures-of-merit are comparable to those of some existing photoactive systems with advantages of simple construction, easy maintenance, and low costs of investment.

1. Introduction

Semiconductor photocatalysis is a sustainable way of treating wastewater containing recalcitrant compounds [1–3], as it offers a clean, solar-driven process. Among semiconductors, zinc oxide (ZnO) is promising for photocatalysis in addition to titanium dioxide (TiO_2), the most widely used semiconductor catalyst. A number of studies show higher photocatalytic activity of ZnO, as compared to that of TiO_2, for degradation of organic compounds under UV [4], visible [5], and solar light [6]. However, similar to other large band gap semiconductors, ZnO only absorbs light in the UV region. Thus, its practical applications are limited.

To extend the spectral response of pristine ZnO to the visible region, doping with N has been shown to be an effective strategy [7–9]. Since the electronegativity of N is lower than that of O, a new energy level within the band gap can be formed by N [9]. During the doping process, additional energy levels may also be introduced due to the formation of structural defects, such as oxygen vacancies. These new energy levels allow multiple electron excitations, leading to an extended spectral response. They can also act as electron traps, resulting in enhanced photocatalytic activity.

Photocatalytic degradation of recalcitrant compounds by N-doped ZnO (N-ZnO) in slurry systems has been studied [10,11]. However, from a practical viewpoint, recovering the used catalysts is a challenging task, as it requires long settling times for sedimentation and can be expensive for filtration. Light scattering by catalyst particles is also another issue in a slurry system.

To avoid post separation of catalyst particles, catalyst immobilization on a stationary, solid support is promising. A variety of supporting materials have been employed, including stainless steel mesh [12], polyacrylic film [13], glass beads [14], Perlite granules [15], Pumice stones [16], pebbles [17], Cuddapah stones [18], and porous silica [19]. Recently, textile fabrics, made from cotton [20], flax [21], nylon [22], and polyester [23], have also been proposed as suitable catalyst supports due to their flexibility, relative stability, and low-cost. Of these different fabric types, polyester fabrics seem to be preferable due to their strength, combined with their resistance to UV and chemicals [24].

The purpose of this research is to develop a solar photoactive system (N-ZnO@PF), consisting of N-doped ZnO nanoparticles immobilized on a polyester fabric (PF). Several photoactive systems consisting of metal oxide catalysts immobilized on textile fabrics have been developed [25–29]. There are two main issues noticed on the immobilization of catalyst particles, namely, (i) poor attachment of catalyst particles and (ii) cracking of catalyst particle films. These lead to loss of catalyst particles during photocatalytic operation. To avoid such problems, protective layer and/or binder can be introduced. These additional compounds can also protect the immobilized catalyst particles from reactive species attack

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during irradiation. However, the surface area of the catalyst particles exposed to incoming light is decreased and the binder itself might be degraded by the reactive species. For these reasons, in this research, the N-ZnO particles are immobilized on a PF without binder or protective layer. To improve the immobilization of the catalyst particles on the PF surface, simple pretreatment of PF with alkali is employed since it has been proven effective for increasing hydrophilicity of textile fabrics [24,30,31]. Alkali treatment was shown to alter the chemical, physical, and morphological properties of a fabric by increasing the amount of surface functional groups, improving the accessibility of functional groups on the newly exposed surfaces, and increasing the roughness and porosity of the surface [24]. The alkali treatment of the PF is then followed by treatment with UVC light to induce the formation of chelating agents on the PF surface which can bind the catalyst particles [32,33]. The photocatalytic activity of N-ZnO@PF is evaluated for the degradation of amaranth (AM), a recalcitrant organic compound, under solar light with a thin-film fixed-bed reactor (TFFBR). The effects of inorganic ions on the AM degradation is also studied. The IUPAC figures-of-merit of the photoactive system N-ZnO@PF are estimated and compared with those of some existing photoactive systems.

2. Materials and methods

2.1. Materials and chemicals

An undyed 100% polyester fabric, obtained from a local market, was used. All chemicals were of analytical grade. Zinc acetate dihydrate ($Zn(O_2CCH_3)_2{\cdot}2H_2O$), Ajax), urea ($CO(NH_2)_2$, Merck), amaranth ($C_{20}H_{11}N_2Na_3O_{10}S_3$, Aldrich), sodium chloride (NaCl, Chameleon reagent), sodium nitrate ($NaNO_3$, Aldrich), sodium carbonate (Na_2CO_3, Chameleon reagent), sodium sulfate (Na_2SO_4, Chameleon reagent), and calcium sulfate ($CaSO_4$, Chameleon reagent) were used as received without further purification. DI water was used in all of the processes.

2.2. Synthesis of N-ZnO

N-ZnO was obtained through a new, simple route of synthesis based on mechanochemical process with liquid-assisted grinding. Zinc acetate dihydrate (2.19 g) and urea (1.2 g) in a 1:2 molar ratio were ground in an agate mortar for 30 min at room temperature to obtain a paste of zinc acetate-urea. Before grinding, 1 mL of water was added to make the resulting mixture uniform. The ground mixture was calcined at 500 °C for 3 h in a muffle furnace. The obtained powders of N-ZnO were washed with water followed by ethanol prior to drying in an oven at 100 °C for 24 h. The dried powders were then ground in the agate mortar and kept in a desiccator for further use.

2.3. Preparation of N-ZnO@PF

To remove impurities, PF having a size of 20 cm × 20 cm was scoured with detergent at 80 °C for 30 min, followed by rinsing with a large amount of water. After being cleaned with acetone at room temperature for 30 min, the fabric was immersed in 1 M of NaOH solution at 80 °C for 2 h, repeatedly rinsed with water, and dried at 80 °C for 24 h. Subsequently, the alkali-treated fabric was irradiated with UVC light at room temperature for 5 h, immersed in 16 g/L of N-ZnO suspension at room temperature for 24 h under agitation on a shaking bath at 200 rpm, and dried at 80 °C for 24 h. Before immersion, the N-ZnO suspension was sonicated in an ultrasonic bath for 2 h to deagglomerate the N-ZnO particles. Immersion-drying was undertaken five times in succession. The coated fabric was furthermore subjected to heating at 200 °C for 30 min. To remove weakly attached particles, it was rinsed with water followed by drying at 80 °C for 24 h. The average catalyst loading on the PF surface is found to be 13.5 g/m^2.

2.4. Characterization of N-ZnO@PF

The infrared spectra were recorded by a Fourier transform infrared (FTIR) spectrometer (Nicolet 6700) in attenuated total reflection (ATR) mode for functional group elucidation. X-ray diffraction (XRD) patterns were collected on a Bruker D8 diffractometer (Cu Kα radiation, $\lambda = 1.5406$ Å). Morphological properties were observed by scanning electron microscopy (SEM) (S-3400N, Hitachi) and transmission electron microscopy (TEM) (JEM 2100, Jeol). Diffuse reflectance spectra (DRS) were obtained from a UV–vis-NIR spectrophotometer (Cary 5000, Agilent). The chemical state of N dopant was verified by X-ray photoelectron spectroscopy (XPS) (Axis Ultra DLD, Kratos Analytical) with Al Kα radiation and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy at Beamline 3.2a of the Synchrotron Light Research Institute (Public Organization), Thailand.

2.5. Photocatalytic activity evaluation

A TFFBR in recirculation mode, consisting of a covered reservoir, a peristaltic pump, and a sloping plate for collecting light, was used (Fig. 1). The N-ZnO@PF was attached to the sloping plate having a workable area of 20 cm × 20 cm. An AM solution with a volume of 0.5 L was transferred into the reservoir. The pH of the AM solution was adjusted to the desired level using dilute NaOH and HCl. The AM solution falls as a thin film from the top of the plate, allowing effective oxygen transfers from the air into the solution film. To initiate a photocatalytic reaction, the system was then irradiated with solar light at ambient temperature between 9:00 a.m. and 3:00 p.m. during the months of August to October (Khlong Luang, Thailand; latitude 14°3′N and longitude 100°38′E). The solar irradiance was measured regularly during the experiments at the same angle as that of the sloping plate at five different points across the length and breadth of the sloping plate. The average solar irradiance was found to be 685.1 W/m^2. After a given irradiation time, the solution was withdrawn and centrifuged to measure its absorbance at λ_{max} of 521 nm using a UV–vis spectrophotometer. No interference in absorbance is found at this wavelength as no peak shift is observed. Therefore, the measurement is reliable. To determine the AM concentration, calibration plots based on Beer-Lambert's law were established by relating the absorbance to the concentration. The dye degradation efficiency (*DE*) was calculated from the equation:

$$DE(\%) = \left(\frac{C_0 - C}{C_0}\right) \times 100 \quad (1)$$

where, C_0 and C are the initial and final concentrations of AM in the solution (mg/L), respectively.

Control experiments with solar light in the absence of N-ZnO@PF were carried out for 6 h. AM is found to be stable under the experimental conditions applied, resulting in photolysis of less than 12%. In the absence of solar light, insignificant adsorption of AM by N-ZnO@PF was observed. At equilibrium, which was attained within about 30 min, less than 7% of AM was adsorbed. It is seen that AM was mainly removed through photocatalysis.

To study the effect of operating parameters, experiments were performed by varying key operating parameters, namely, AM concentration (5–25 mg/L), pH (5–9), plate inclination (20–40°), flow rate (80–120 mL/min), salinity (1.2–4.8 g/L of NaCl), and inorganic ions (Ca^{2+}, CO_3^{2-}, SO_4^{2-}, and NO_3^- with a concentration of 0.05 M). DI water was circulated for 30 min to clean the system