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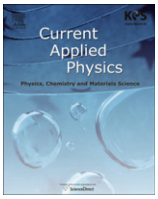

Preparation and photocatalytic degradation of erbium doped titanium dioxide nanorods

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ABSTRACT

Photocatalytic degradation of methylene blue (MB) in water was examined using Er^{3+}-doped TiO_2 (Er–TiO_2) nanorods prepared by a sol–gel derived electrospinning, calcination, and subsequent mechanical grinding. Different concentrations of Er dopant in the range of 0–1.0 mol% were synthesized to evaluate the effect of Er content on the photocatalytic activity of TiO_2. Among Er^{3+}–TiO_2 catalysts, the 0.7 mol% Er^{3+}–TiO_2 catalyst showed the highest MB degradation rate. The degradation kinetic constant (k) increased from 1.0×10^{-3} min^{-1} to 5.1×10^{-3} min^{-1} with the increase of Er^{3+} doping from 0 to 0.7 mol%, but decreased down to 2.1×10^{-3} min^{-1} when Er^{3+} content was 1.0 mol%. It can be concluded that the degradation of MB under UV radiation was more efficient with Er^{3+}–TiO_2 catalyst than with pure TiO_2. The higher activity might be attributed to the transition of 4f electrons of Er^{3+} and red shifts of the optical absorption edge of TiO_2 by erbium ion doping.

1. Introduction

TiO_2-based thin film photocatalysts have been investigated extensively for environmental applications such as air, water treatment and deodorizer, because of its strong oxidizing power, high photocatalytic activity, self-cleaning function, bactericidal and detoxification activity [1–3]. TiO_2 under ultraviolet (UV) illumination has been proposed as the most effective and advanced removal alternative for environmental and biomedical applications due to its efficiency of electron–hole pair separation and its optical absorption property [2]. TiO_2 under UV radiation can be excited to generate charges leading to the production of oxidative radicals, which can mineralize organic pollutants into carbon dioxide and water [4–6]. The suitable doping has exhibited the enhancement of photoactivity of doped TiO_2 [3]. Among them, a lanthanide-modified TiO_2 by doping may effectively eliminate the electron–hole recombination in the photocatalytic reaction. Lanthanide (rare earth) ions are likely to form complexes with various Lewis bases (e.g., acids, amines, aldehydes, alcohols, thiols, etc.) in the interaction of these functional groups with the f-orbital of the lanthanides [2–8]. The incorporation of lanthanide ions into TiO_2 matrix may adsorb dramatically the organic pollutants at the semiconductor surface and facilitate the degradation of organic pollutants [2,3]. In addition, the fibrous catalyst has a 3-D interconnected open structure which is beneficial for the photocatalytic reactions [9].

Pure TiO_2 had no absorption in the visible light region (>400 nm), however, Er^{3+}–TiO_2 showed typical absorption peaks located at 490, 523 and 654 nm, corresponding to the transition of 4f electrons from $^4I_{15/2}$ to $^4F_{7/2}$, $^2H_{11/2}$ and $^4F_{9/2}$, respectively [2–4,7,8]. Er doping may cause the red shift of absorption edge of TiO_2, leading to improved visible light photocatalytic activity of TiO_2. Visible light irradiated photocatalytic activity of Er^{3+}–TiO_2 was near twice as much as that of pure of TiO_2 and the UV irradiated photocatalytic activity of Er^{3+}–TiO_2 was near threefold as much as that of pure TiO_2 [2–4]. In the textile dyes, 15% is lost during the dying process out of the world production of dyes and is released in the textile effluents [3,5]. These effluents contain azo dyes and huge amount of inorganic salts. Among the textile dyes, methylene blue (MB, $C_{16}H_{18}ClN_3S_3$) is a brightly colored blue cationic thiazine dye with λ_{max} at 665, 614, 292 nm [3]. In the present study, Er^{3+}–TiO_2 catalysts were synthesized by a sol–gel derived electrospinning and subsequent calcination. The photocatalytic degradation of MB by the Er–TiO_2 photocatalysts was examined as a function of dopant content by using an UV/vis spectrophotometer.

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2. Experimental

The precursor solution was prepared from 3.5 g of titanium tetrabutoxide ($Ti[O(CH_2)_3CH_3]_4$, 97%, Aldrich, USA) in 3 g of acetic acid by stirring. Polyvinylpyrrolidone (0.45 g, PVP, Mw = 1,300,000, Aldrich, USA) dissolved in 5.5 g of ethanol was added to the TiO_2 precursor solution. Then, erbium chloride ($ErCl_3$, Aldrich, USA) was added into the above solution to obtain Er^{3+}–TiO_2 [7,8].

The electrospinning apparatus consisted of a syringe pump (KDS-200, Stoelting Co., USA), a 22-gage BD metal needle, a grounded collector, and a high-voltage supply (ES30P-5W, Gamma High Voltage Research Inc., USA) equipped with current and voltage digital meters. The solution was placed in a 5 mL BD Luer-Lok syringe attached to the syringe pump and fed into the metal needle at flow rate of 0.3 mL/h. The grounded collector was a stainless mandrel placed 12 cm from the tip of the needle. The drum enveloped with a piece of aluminum foil was rotated at 300 rpm to collect the Er^{3+}–TiO_2 nanofibrous film under a DC voltage of 10 kV. A piece of flat aluminum foil was placed 12 cm below the tip of the needle to collect the nanofibers. The as-spun nanofibers were dried in air for 5 h to allow the hydrolysis. Subsequent annealing for 3 h at 500 °C in air with a heating rate of 1 °C/min was performed [8]. The nanofibers were ground mechanically in a pestle and mortar to produce nanorods, as shown in Fig. 1 [10,11].

The precursor solutions were characterized by measuring the viscosity and the surface tension. The kinematic viscosity, the surface tension, and the density of the precursor solution were determined by using a Cannon-Fenske viscometer, a dynamic tensiometer (Nima, DST9005, USA) and a pycnometer, respectively. The dynamic viscosity was calculated from the kinematic viscosity and the density data. The diameter and the morphology of the nanofibers were evaluated using SEM (Hitachi S-3000H, Japan) and TEM (JEM-2000EX, Jeol, Japan). All specimens were coated with Au/Pd to ensure higher conductivity. For the SEM observation, the Er–TiO_2 nanofibers were prepared by placing silicon wafers on the aluminum foil during electrospinning. The crystalline phase of the nanorods was analyzed by using an XRD (Mac Science, KFX-987228-SE, Japan). UV/vis absorbance spectra of the Er–TiO_2 nanofibrous films in the 200–700 nm region were obtained by using a spectrometer (Jasco V-670, Japan).

A pyrex cylindrical photoreactor enclosed by a blackbody was used in the experiment, as shown in Fig. 2. A 9-W medium-pressure mercury lamp with a main emission peak at 365 nm (Philips, PL-S 9W/10/2P, Holland) was positioned at the center of the cylindrical vessel with a circulating water jacket to control the temperature at 25 ± 1 °C during the reaction. The reaction suspension was prepared by adding 0.1 g of photocatalyst (0.2 g/L) into 500 mL of MB (Daejung Chemicals & Metals Co., Korea) solution with a concentration of 10 mg/L. Prior to photocatalytic oxidation, the suspension was stirred in a dark condition for 120 min to establish adsorption and desorption equilibrium, which was considered as the initial concentration (C_o) after dark desorption. The aqueous suspension containing MB and photocatalyst was irradiated under UV illuminated with constant aeration. Air at a flow rate of 2 L/min was bubbled through the reaction solution from the bottom to ensure a constant dissolved oxygen concentration [12,13]. At the given time intervals, the analytical samples were taken regularly from the suspension and immediately centrifuged at 2000 rpm for 20 min, then filtered through a 0.45 μm Millipore filter to remove the particles. The change of adsorption at 664 nm was applied to identify the concentration of MB using an UV/vis spectrophotometer and the concentration of MB was measured as a function of irradiation time [2,3,5,6].

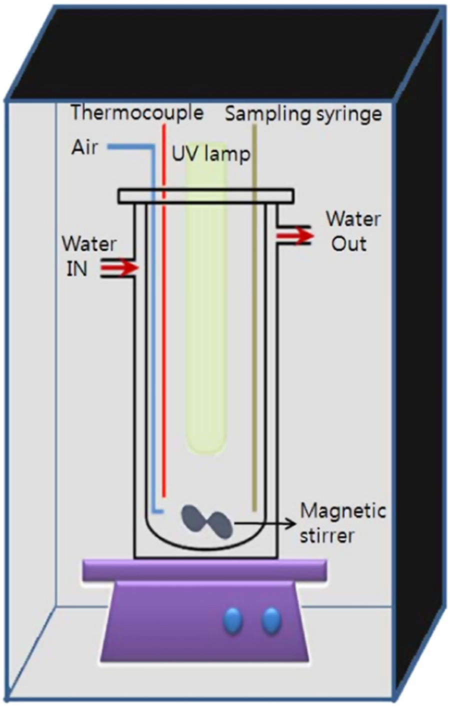

Fig. 2. A schematic diagram of the photoreactor apparatus.

3. Results and discussion

The dynamic viscosity and surface tension of TiO_2 solution are determined to be 32 cP and 22.7 mN/m, respectively. Rheological

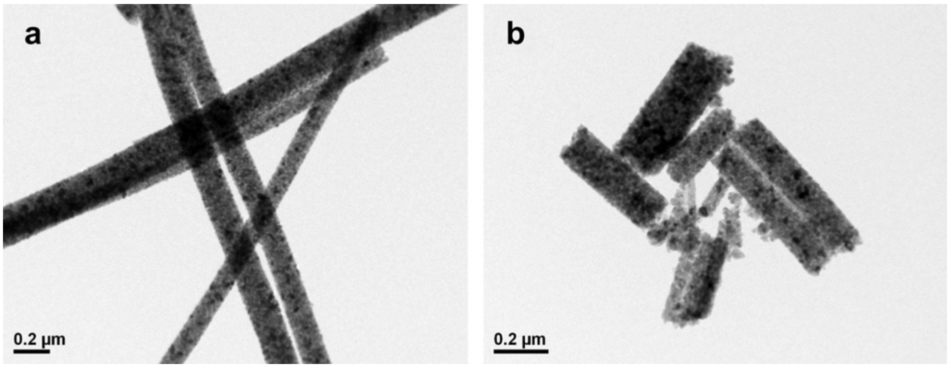

Fig. 1. TEM images of Er^{3+}–TiO_2 nanofibers (a) before and (b) after grinding.