

Effect of calcination temperature on photocatalytic activities of Er-TiO₂ nanotubes

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0.7 mol% Er-TiO₂ nanotubes were prepared using a sol-gel derived electrospinning and subsequent calcination at intervals of 50 °C from 500 °C to 650 °C to investigate the effect of calcination temperature on the crystal structure and the photocatalytic activity of methylene blue (MB). X-ray diffraction (XRD) results indicated that Er-TiO₂ nanotubes calcined at 500 °C were composed of anatase only. However, mixed phases of anatase (51%, 55%, 96%) and rutile (49%, 45%, 4%) were observed for the nanotubes calcined at 550 °C, 600 °C and 650 °C, respectively. As the calcination temperature rose from 500 °C to 600 °C, the Barrette-Emmett-Teller (BET) surface area and degradation kinetic constant increased from 97.77 m²/g to 117.62 m²/g and from $1.2 \times 10^{-2} \text{ min}^{-1}$ to $1.6 \times 10^{-2} \text{ min}^{-1}$, respectively. The Er-TiO₂ nanotubes calcined at 600 °C exhibited enhanced MB degradation (87%) compared to that of Er-TiO₂ nanofibers (37%) due to the synergic combinations of tailored mixed crystals and larger BET area.

Key words: Er-doped TiO₂, Electrospinning, Nanotube, Methylene blue, Photodegradation.

Introduction

The photocatalytic degradation of organic pollutants by using metal-doped TiO₂ has been examined as a function of the dopant content. A suitable metal doping (Co, Fe, Mn, Zn, Er, Pt, Nb, Al) has been found to improve the photocatalytic reaction efficiency [1-10]. Among them, Er-doped TiO₂ may effectively extend the absorption of TiO₂ in the visible region and enhance the photocatalytic activity of TiO₂ under solar irradiation [5,9,10]. The substitution of Er³⁺ (0.103 nm) for Ti⁴⁺ (0.0605 nm) distorts the structure due to the smaller ionic size of Ti⁴⁺ and the charge imbalance [5]. The undoped TiO₂ nanofibers calcined at 500 °C consisted of pure anatase phase [11, 12], and the anatase peak became weaker with increasing the Er content from 0 mol% to 1.5 mol%, indicative of a reduced grain size and a lower extent of crystallinity [9,10]. The crystallite size decreased due to the hinderance of the crystallite growth as a result of segregation of the dopant cations at the grain boundary [9]. Among Er-TiO₂ nanofibers, the 0.7 mol% Er-TiO₂ catalyst showed excellent methylene blue (MB) degradation rate and degradation kinetic constant (*k*) of $5.1 \times 10^{-3} \text{ min}^{-1}$ mainly due to the transition of 4f electrons of Er³⁺ and red shifts of the optical

absorption edge of TiO₂ by erbium doping [9]. UV-vis spectrophotometer showed that the values of optical indirect band gap energy (*E_g*) decreased from 3.25 eV to 2.81 eV with the increase of Er doping from 0 to 0.7 mol%, but changed to 2.89 eV when Er content was 1.0 mol%. The reduction in *E_g* may be attributed to electron and/or hole trapping at the donor and acceptor levels in the TiO₂ band structure [10]. Further doping above 0.7 mol% of Er was detrimental to the photodegradation of MB [9].

Er-TiO₂ nanotubes with excellent specific surface area were prepared to increase the photodegradability of MB. The nanotubes with internal hollow structures, which were electrospun using double nozzles, exhibited excellent specific surface area. Although Er-TiO₂ nanofibers exhibited the photodegradation enhancement of MB as a function of Er content, few studies regarding the Er-TiO₂ nanotubes possessing higher specific surface areas have been researched [5, 9, 11, 12]. In the present study, the TiO₂ nanotubes doped with 0.7 mol% Er³⁺ ions were electrospun by varying the calcination temperature to investigate a photocatalytic activity of MB. The photocatalytic activity of MB was examined by using a pyrex photoreactor and an UV-vis spectrophotometer to evaluate the effect of calcination temperature (500 °C to 650 °C) on the crystal structure and the photocatalytic activity of the 0.7 mol% Er-TiO₂ nanotubes.

Experimental Procedure

The precursor solution was prepared from 0.28 g of

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polyvinylpyrrolidone (PVP, Mw=1,300,000, Aldrich, USA) in a mixture of ethanol and acetic acid by stirring for 15 min at 350 rpm [5, 9]. 3.5 mL of titanium tetrabutoxide (Ti[O(CH₂)₃CH₃]₄, 97%, Aldrich, USA) was added to the TiO₂ precursor solution and stirred for 25 min at 500 rpm. Then, erbium chloride (ErCl₃, Aldrich, USA) was added to the above solution to obtain 0.7 mol% Er-TiO₂ solution by stirring for 1 hr at 650 rpm. The solution viscosity and surface tension were measured at room temperature using a viscometer (DV 1M, Brookfield, USA) with spindle NO. SC4-31 at 50 rpm and a dynamic tensiometer (Nima, DST9005, USA), respectively [13, 14].

Er-TiO₂ nanotubes were prepared by electrospinning two immiscible liquids through a dual concentric nozzle (17G-23G), followed by selective removal of the cores. Two immiscible liquids were injected at appropriate flow rates through two concentrically located needles. In the preparation of Er-TiO₂ nanotubes, the feeding rates for heavy mineral oil (Sigma-Aldrich, USA) and sol were 1.0 mL/h and 0.33 mL/h, respectively. The electric field was 1.67 kV/cm. Hollow nanotubes were obtained by immersing the as-spun fibers in octane (CH₃(CH₂)₆CH, Sigma-Aldrich, USA) and subsequent calcination for 3 hrs at temperatures from 500 °C to 650 °C.

A photocatalytic experiment was performed on MB (Daejung Chemicals & Metals Co., Korea) in a pyrex photoreactor enclosed by a blackbody. The process is described in detail elsewhere [7-9,12]. The reaction suspension was prepared by adding 0.1 g of photocatalyst (0.2 g/L) into 500 mL of MB solution with a concentration of 10 mg/L. The aqueous suspension containing MB and photocatalyst was irradiated under UV illuminated (365 nm) with constant aeration (2 L/min). The microstructure of the nanotubes was evaluated using a transmission electron microscope (TEM, JEM-2000EX, Jeol, Japan). The crystalline phase of the films was analyzed by using an X-ray diffraction (XRD, Mac Science, KFX-987228-SE, Japan). The change in the adsorption at 664 nm was applied to identify the concentration of MB by using an UV-vis spectrophotometer (V-670, Jasco, Japan), and the concentration of MB was measured as a function of irradiation time [7-9].

Results

Our previous studies revealed that the 0.7 mol% Er-TiO₂ nanofibers exhibited the best catalyst for the photodegradation of MB due to the transition of 4f electrons (from ⁴I_{15/2} to ⁴F_{7/2}, ²H_{11/2} and ⁴F_{9/2}) of Er³⁺ and the red shifts of the optical absorption edge of TiO₂ by erbium ion doping [5]. The values of energy gap (E_g) decreased dramatically from 3.25 eV to 2.81 eV with the increase of Er doping from 0 to 0.7 mol% due to electron and/or hole trapping at the donor and acceptor levels in the TiO₂ band structure [10]. The lowest E_g was in good

agreement with the photodegradation results (~50%) of Er-TiO₂ nanofibers for MB in water [9]. The rheological properties of 0.7 mol% Er-TiO₂ solution were examined. The Er-TiO₂ solution's viscosity and surface tension were determined to be 12 cP and 20.1 mN/m, respectively.

The thermal decomposition behavior of Er-TiO₂ nanotubes is shown in Fig. 1. The weight loss in the TG curve occurred until 507.7 °C. The endothermic peaks at 80.1 °C and 383.5 °C in the DSC curve may be attributed to the evaporation of water and the polymer decomposition. The exothermic peaks at 328.2 °C and 472.9 °C were observed. Dramatic weight losses (29.68%) occurred around 120 °C due to the decomposition of organic groups. Another exothermic peak at 472.9 °C may correspond to the formation of the TiO₂ phase. The TG/DSC results revealed that most of the organic groups were vanished approximately at ~507 °C.

XRD results of the Er-TiO₂ nanotubes were shown in Fig. 2. The anatase-to-rutile ratio was calculated according to Parida and Sahu [15], % of anatase phase = $100 / \{1 + (I_R / 0.79 I_A)\}$, where I_A and I_R are the

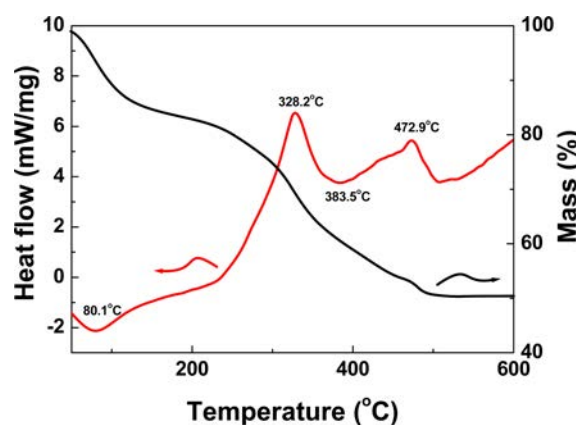


Fig. 1. TG/DSC curves of the electrospun Er-TiO₂ nanotubes.

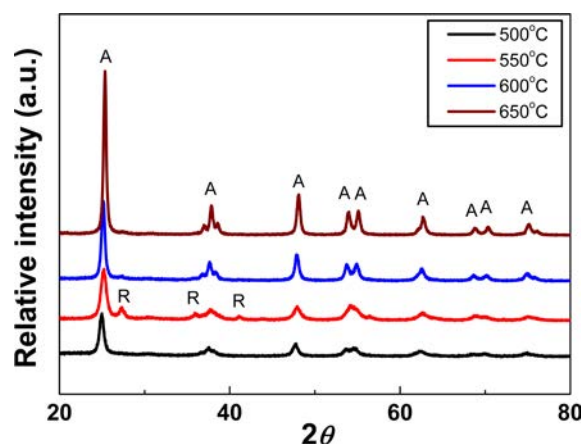


Fig. 2. XRD patterns of Er-TiO₂ nanotubes calcined at various temperatures.

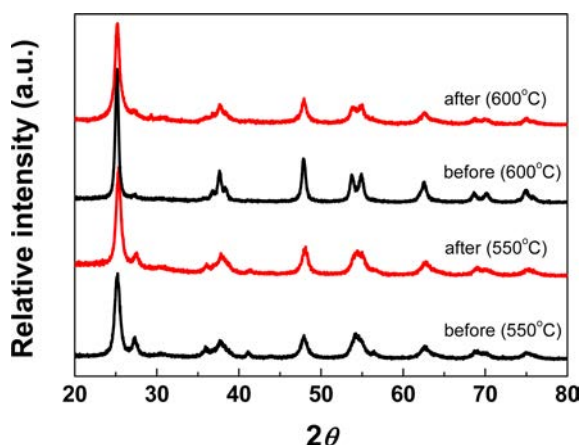


Fig. 3. XRD patterns of the calcined Er-TiO₂ nanotubes before and after the photodegradation test of methylene blue.

intensities of the strongest diffraction line (101) of the anatase phase and the (110) line of the rutile phase, respectively. Er-TiO₂ nanotubes calcined at 500 °C consisted of the anatase phase. However, mixed phases of anatase and rutile were observed for the Er-TiO₂ nanotubes calcined at temperatures more than 550 °C. The ratios of anatase to rutile phases for the Er-TiO₂ nanotubes calcined at 500 °C, 550 °C, 600 °C, and 650 °C were 100/0, 51/49, 55/45, and 96/04, respectively. The extent of the anatase-to-rutile phase transformation increased dramatically from 0% to 49% when the calcination temperature rose from 500 °C to 550 °C. In addition, no structural changes (ratio of anatase to rutile) of Er-TiO₂ nanotubes calcined at 550 °C and 600 °C were detected after the photodegradation experiment, as depicted in Fig. 3. However, the fraction of rutile phase decreased significantly from 49% to 4% as the calcination temperature increased from 550 °C to 650 °C.

Energy dispersive X-ray spectrometer (EDS) results for the Er-TiO₂ nanotubes (Fig. 4) suggested that Er-TiO₂ had successfully been formed. Er species dissolved well into the TiO₂ crystals by the substitution

of Er³⁺ for Ti⁴⁺ due to the similar ionic sizes of Er and Ti [5]. It is reported that a substitution of Ti⁴⁺ ions by Er³⁺ in the TiO₂ lattice resulted in the distortion, the expansion of crystal lattice, and the charge imbalance (Ti⁴⁺ + e⁻ → Ti³⁺). Ti³⁺ on the surface is oxidized by molecular oxygen to form the superoxide anion (O₂⁻), (Ti³⁺ + O₂(gas) → Ti⁴⁺ + O₂⁻), and holes (h⁺) trapped by superoxide anion lead to the formation of OH radical (OH[·]). When the photocatalytic oxidation is performed in aqueous medium, the holes (h⁺) were effectively scavenged by the water and generated hydroxyl radicals (OH[·]) which oxidize adsorbed molecules, (h⁺ + H₂O → OH[·] + H⁺). The superoxides and the hydroxyl radicals may act as active reagents for the mineralization of the organic components [9]. The recombination rate of electron and hole pairs may be reduced dramatically, leading to a positive influence on the photocatalytic activity of Er-TiO₂ [9, 10].

The extent of the anatase-to-rutile phase transformation for the TiO₂ nanotubes was 24% [8]. It increased dramatically from 24% to 57% when Al was doped into TiO₂. Higher degree of the anatase-to-rutile phase transformation was effective in the photodegradation of MB due to the formation of multiphase type-II heterojunctions and excellent BET surface area. The specific surface area was determined by using the Barrette-Emmett-Teller (BET) method (ASAP 2010, Micromeritics, USA). A catalyst with a larger surface area has been known to exhibit better adsorption capacity [8, 12]. The Al-TiO₂ nanotubes possessing mixed phases showed higher BET area of 151.08 m²/g compared to that (34.21 m²/g) of TiO₂ nanotubes [8]. In the present study, the extent of the anatase-to-rutile phase transformation for the Er-TiO₂ nanotubes calcined at 550 °C and 600 °C was 49% and 45%. And the BET surface areas were 107.63 m²/g and 117.62 m²/g, respectively. These Er-TiO₂ nanotubes exhibited better BET area than that (35.36 m²/g) of Er-TiO₂ nanofiber as expected. The crystallite size of anatase and rutile Er-TiO₂ determined by the Scherrer formula, are listed in Table 1. The lowest crystallite size for the

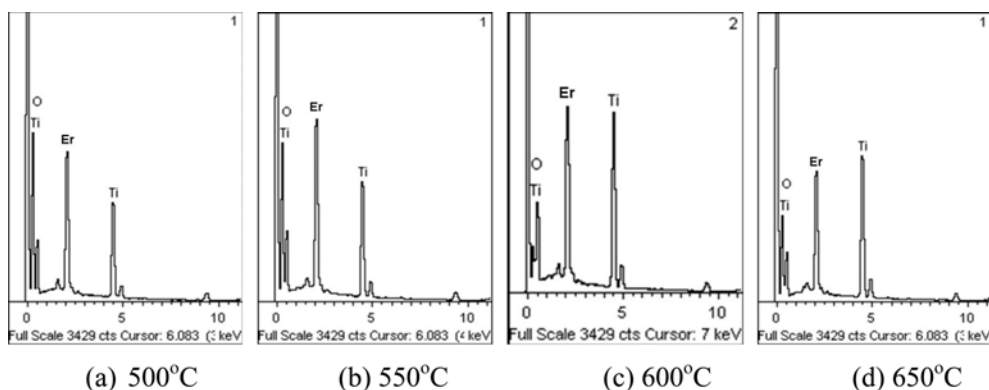


Fig. 4. EDS results of Er-TiO₂ nanotubes calcined at various temperatures.

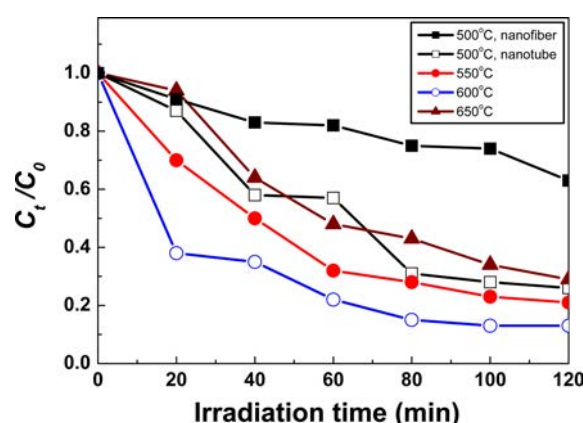
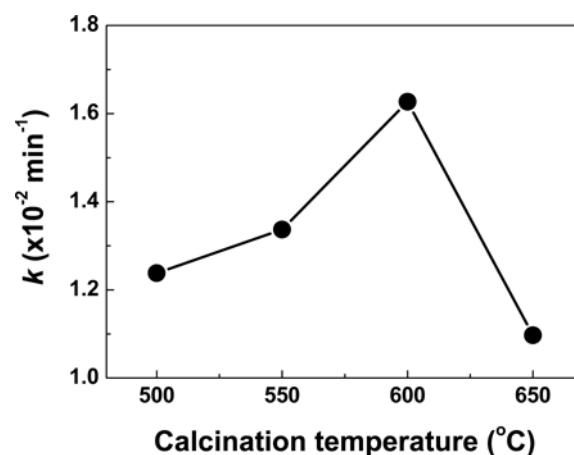
Table 1. Properties of Er-TiO₂ nanotubes calcined at various temperatures.

Calcination temperature (°C)	Phase	Phase content (%)	Crystallite size (nm)	BET surface area (m ² /g)
500	Anatase only	100/0	11.3/-	97
550	Anatase/rutile	51/49	8.9/9.0	107.63
600	Anatase/rutile	55/45	6.3/21.5	117.62
650	Anatase/rutile	96/04	5.0/27.8	130.20

anatase (5.0 nm) was observed for the Er-TiO₂ nanotubes calcined at 650 °C, resulting in the largest BET surface area (130.20 m²/g). A smaller crystallite size may correspond to a larger surface area, which is consistent with the BET results. It is conceivable that the large BET area and the optimal crystallinity are likely to have an effect on the photocatalytic activity due to an increase in the number of active sites for photocatalytic reactions [8].

The photocatalytic activities of Er-TiO₂ catalysts were investigated by using the photodegradation of MB under UV light (365 nm), as depicted in Fig. 5. After 120 min of UV irradiation and aeration with Er-TiO₂ nanofibers calcined at 500 °C, a 37% degradation of MB at 664 nm was derived from the absorbance measurements and is most likely due to the adsorption of dye molecules on the surface of anatase TiO₂ [7-9]. The extent of MB degradation increased to 74% when Er-TiO₂ nanotubes were synthesized. This may be due to a increase in BET surface area from 35.36 m²/g to 97.77 m²/g (Table 1). The photodegradation of MB due to Er-TiO₂ nanotubes calcined at 600 °C increased dramatically to 87%. The BET area (117.62 m²/g) was increased 3 times higher than that (35.36 m²/g) of Er-TiO₂ nanofiber. The higher degradation of MB may be due to the synergic combination of mixed crystals (anatase and rutile) and larger BET area. The extent of the photodegradation of MB decreased from 87% to 75% when the nanotubes were calcined at 650 °C. It may be due to the dramatic reduction in the rutile phase fraction from 45% to 4%. However, the physical mechanisms involved are not yet completely understood.

Fig. 6 shows a plot of (C_t/C_o) versus time (t), where C_o and C_t are the initial concentration of MB and the concentration at any time t, respectively. Because all the curves could be fitted roughly to an exponential relation. The degradation kinetics of MB for various Er-TiO₂ catalysts under UV light can be analyzed by using a pseudo-first-order kinetic model [7-9, 12]. A Langmuire-Hinshelwood type of kinetic model, $-\ln(C_t/C_o) = k_r K_a t = kt$, where k_r , K_a and k are, respectively, the degradation kinetic constant, the adsorption equilibrium constant, and the apparent kinetic constant (min⁻¹) [7-9]. The apparent kinetic constant (k) has been reported to show a behavior similar to that of the degradation constant (k_r), suggesting that the adsorption played an

**Fig. 5.** The photodegradation of MB on different catalysts under UV light.**Fig. 6.** Apparent kinetic constant (k) of MB photodegradation as a function of calcination.

important role in the degradation of MB on Er-TiO₂. The calculated values for the first-order rate constant (k) of Er-TiO₂ nanofibers calcined 500 °C at a 10-ppm MB concentration was found to be $3.4 \times 10^{-4} \text{ min}^{-1}$. The degradation kinetic constants (k) of Er-TiO₂ nanofibers and nanotubes increased from $3.4 \times 10^{-4} \text{ min}^{-1}$ to $1.2 \times 10^{-2} \text{ min}^{-1}$, suggesting that the Er-TiO₂ nanotube was a better catalyst for MB photodegradation. After 120 min of UV irradiation and aeration with Er-TiO₂ nanotubes calcined at 550 °C and 600 °C, 79% and 87% degradations of MB, respectively, were monitored (Fig. 5), and their k values were 1.33×10^{-2} and $1.62 \times 10^{-2} \text{ min}^{-1}$. The k value of the Er-TiO₂ nanotubes calcined at 600 °C was 47 times higher than that of the Er-TiO₂ nanofiber. The improved catalytic activity may be due to the synergic combination of mixed phases and BET surface area [12]. The experimental results suggested that the Er-TiO₂ nanotube calcined at 600 °C was the best catalyst for the photodegradation of MB.

Conclusions

Er-TiO₂ nanofibers and nanotubes (0.38 Al/Ti molar ratio) calcined at temperatures in the range of 500 °C to 650 °C were prepared to evaluate the effect of calcination temperature on the crystal structure and the photocatalytic activity of Er-TiO₂ nanotubes. Although Er-TiO₂ nanotubes calcined at 500 °C possessed only an anatase phase, mixed crystalline phases occurred as the calcination temperature was above 550 °C. In addition, the highest photodegradation of MB was achieved for the Er-TiO₂ nanotubes calcined at 600 °C due to the synergic combination of tailored mixed crystals and larger BET surface area. The calcination temperature was mainly attributed to the crystal structure and the related photocatalytic activity of the Er-TiO₂ catalysts.

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