

Characterization of electrospun TiO₂ nanofibers and its enhanced photocatalytic property under solar light irradiation

Chan-Geun Song, Siva Kumar Koppala and Jong-Won Yoon*

Nano Energy Conversion Materials Laboratory, Department of Advanced Materials Science and Engineering, Dankook University, Cheonan, Chungnam 330-714, Korea

Multiphase TiO₂ nanofibers were fabricated by electrospinning and subsequent calcination of as-spun nanofibers. The obtained TiO₂ nanofibers were characterized by X-diffraction (XRD), Field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). The photocatalytic activity was assessed using methylene blue (MB) degradation in solar light irradiation. With increasing calcination temperature the diameter of the nanofibers decreased. The experimental results of MB degradation demonstrated that the solar light driven photocatalytic activity of TiO₂ nanofibers was enhanced up to 500 °C calcination temperature, and thereafter calcination decreased the photocatalytic activity owing to increase in the rutile phase. A mixed phase (76 : 24) comprised of anatase and rutile phase is more preferable for photocatalysis. The enhanced photocatalytic activity is owing to hindered charge recombination by means of electron transform from anatase phase to rutile phase at trapping states.

Key words: Electrospinning, TiO₂ nanofibers, Methylene blue, Photocatalytic activity.

Introduction

Among the semiconductor metal oxide nanostructures TiO₂ nanostructures have gained much attention in recent years, due to their potential physical properties for various technological applications, including photocatalysis, gas sensors, dye-sensitized solar cells and non-linear optical devices [1-4]. It is well known that photocatalytic reactions always occur on the surface, and are strongly correlated to band gap of the materials, hence a high surface to volume ratio is desired, to improve photocatalytic efficiency [5-7]. In view of this, photocatalysis of one-dimensional TiO₂ nanostructures have recently been reported [8-10].

Numerous methods have been developed for the fabrication of one-dimensional TiO₂ nanostructures, such as self-assembling, template growth, strong alkali treatment, thermal evaporation and electrospinning. Compared to other techniques, electrospinning offers advantages of simplicity, process controllability, low production cost, and scalability for producing industrial quantities [11]. Moreover, electrospinning technique has attracted extensive interest in various areas, including photo-catalysis, gas sensor, lithium-ion batteries, dye-sensitized solar cells, and transparent conductive films [12-16]. Electrospinning technique has been widely used to fabricate different nanostructures (nanobelts,

nanotubes and nanofibers) [17-19].

TiO₂ nanofibers have better photocatalytic efficiencies compared to nanoparticles. Furthermore, TiO₂ nanofiber functional properties depend on both crystalline structure and morphology. The anatase phase is the most preferable for photocatalysis applications [20]. Since, calcination temperature plays a crucial role in phase and crystalline structure transformations, systematic study on calcinations-induced photocatalytic properties is indeed needed. Further, the development of visible light driven photocatalysis is crucial since main part of the solar spectrum can be used and even reduced illumination of interior lighting can also utilized in photocatalysis.

In order to investigate systematic photocatalytic analysis, in the present work we report the fabrication of TiO₂ nanofibers by the electrospinning method. The as-spun nanofibers were calcined at various temperatures. The influence of calcination temperature on the structural and photocatalytic properties of TiO₂ nanofibers was examined under the solar light irradiation.

Experimental

To prepare the precursor solutions for electrospinning, Titanium (IV)-isopropoxide (1.5 ml) was dissolved in a mixture of acetic acid (3 ml) and ethanol (3 ml) and then stirred for one hour to give solution A. Polyvinylpyrrolidone (PVP, MW = 1, 300, 000) (0.675 g) dissolved in ethanol (7.5 ml) was added and stirred for one hour to give solution B. Solution B was added

*Corresponding author:
Tel : +82-41-550-3536
Fax: +82-41-569-2240
E-mail: jwyoon@dankook.ac.kr

Table 1. Physical properties of TiO₂ nanofibers with different calcination temperature.

Calcination Temperature (°C)	Average Diameter of nanofibers (nm)	Anatase phase Crystalline size (nm)	Rutile phase Crystalline size (nm)	Anatase Phase (%)	Rutile Phase (%)
400	350	10	32	71	29
500	278	16	49	76	24
600	205	19	67	4	96
700	155	-	78	-	109

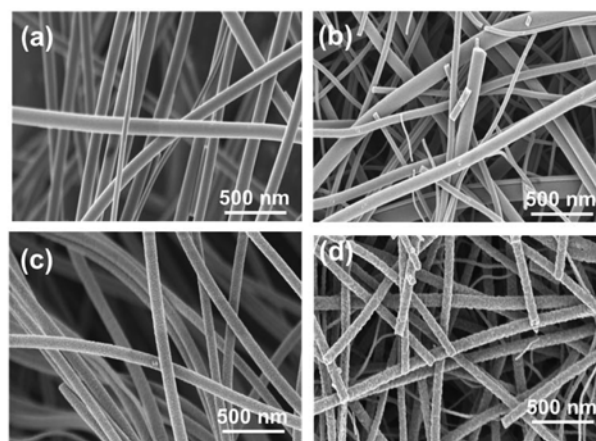
slowly to solution A, and the resulting mixture was further stirred for one hour to get optimized viscosity and suitable volatility. Then PVP-TiO₂ sol precursor was placed into a 10 ml syringe having a metallic needle tip (inner diameter = 0.4 mm) for electrospinning. The solution was fed by a syringe pump. The solution was electro spun at applied voltage 15 kV, flow rate 0.5 µl/sec., and tip-to-collector distance = 15 cm. The as-spun nanofibers were dried overnight under the hood at 80 °C and then calcination took place at 400 °C, 500 °C, 600 °C and 700 °C for 4 h in a furnace in order to obtain crystalline TiO₂ nanofibers.

To determine the crystal phase composition of fabricated TiO₂ nanofibers, we carried out X-ray diffraction measurements using a Rigaku D-max-2500, X-ray diffractometer (Japan) with CuK_α radiation ($\lambda = 0.154$ nm). Scanning electron microscopy images were obtained using a Carl Zeiss Co. (Germany), SPURA60 field emission scanning electron microscope (FESEM). High resolution images of nanofibers were obtained by Carl Zeiss Co. (Germany) EF-TEM, Libra 200FE transmission electron microscope (TEM). To evaluate the photocatalytic activity of TiO₂ nanofibers aqueous methylene blue was used.

Photocatalytic activities of calcined nanofibers were examined by observing the degradation of methylene blue (MB) under solar light (350-750 nm [UV : Vis = 7.8% : 92.2%]) irradiation. The photocatalytic degradation was carried out by mixing 15 mg of the pure TiO₂ nanofibers (calcined at 400 °C, 500 °C, 600 °C and 700 °C) into 100 ml of (10 ppm) methylene blue (MB) aqueous solution under continuous stirring. The experiments were performed at room temperature and prior to irradiation; the slurry was aerated for 45 min to reach adsorption equilibrium followed by solar light irradiation. A 150 W xenon lamp through portable solar simulator (model: PEC-L01, Peccell Technologies) with 120 mW/cm² effective area irradiance was used as a solar light source to trigger the photocatalytic reaction. Aliquots were withdrawn from the suspension at specific time intervals. The absorbance of the MB solution was measured with a UV-optizen 3220UV, Mecasys (Korea) spectrophotometer.

Results and Discussion

Figure 1 shows FESEM images of as-spun TiO₂

**Fig. 1.** SEM images of TiO₂ nanofibers calcined at (a) 400 °C, (b) 500 °C, (c) 600 °C and (d) 700 °C.

nanofibers and calcined TiO₂ nanofibers at 400 °C, 500 °C, 600 °C and 700 °C. Smooth injection of fine TiO₂ sol dispersed in the polymer matrix during electrospinning was evident from all individual nanofibers with preserved cross-sectional consistency throughout the length. The average diameter of, 400 °C, 500 °C, 600 °C and 700 °C calcined TiO₂ nanofibers were of 350 nm-155 nm (shown in Table 1). Compared to the average diameter of as-spun TiO₂ nanofibers, the average diameter of calcined TiO₂ nanofibers was decreased with increase in calcining temperature owing to decomposition of the PVP polymer. The roughness of the nanofibers increased with increasing calcining temperature due to increase in grain size.

Figure 2 demonstrates XRD patterns of the as-spun and calcined TiO₂ nanofibers. It is evident from Figure 2 that the calcination temperatures used in the present study are ample to decompose the polymeric component (PVP), and to obtain the polycrystalline TiO₂ nanofibers. Diffraction peaks are indexed as those originating from tetragonal anatase and rutile phases of TiO₂. The peaks located at $2\theta = 25.2^\circ, 38.5^\circ, 48.0^\circ, 53.8^\circ$ and 55.0° elucidate the diffraction of (101), (112), (200), (105) and (211) anatase TiO₂ (JCPDS 21-1272), and the peaks located at $2\theta = 27.3^\circ, 36.0^\circ, 39.1^\circ, 41.2^\circ, 44.0^\circ, 54.3^\circ, 56.6^\circ, 62.7^\circ, 64.0^\circ, 69.0^\circ$ and 69.7° are indexed as the (110), (101), (200), (111), (210), (211), (220), (002), (310), (301) and (112) planes of rutile TiO₂ (JCPDS 21-1276). As the calcination temperature increases from 400 °C to 700 °C, the anatase phase

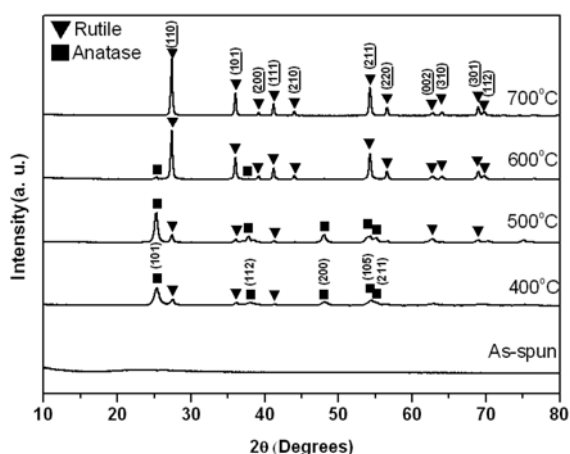


Fig. 2. XRD patterns of TiO₂ nanofibers heat treated at various calcining temperatures.

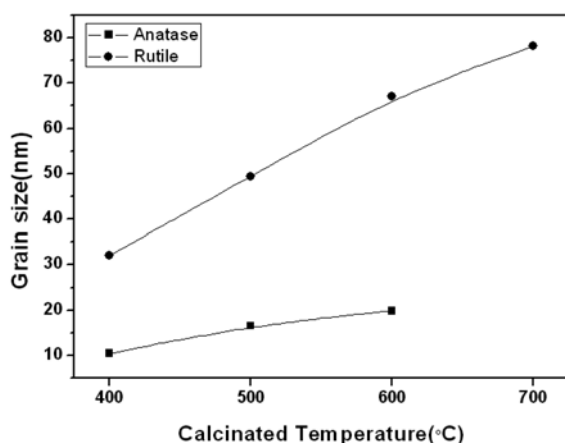


Fig. 3. Variation of grain size with calcining temperature.

becomes sharper up to 500 °C, and thereafter, rutile peaks became sharper and narrow, indicating improvement in the crystallinity of the anatase phase up to 500 °C, and thereafter rutile TiO₂ phases. After 600 °C pure rutile phase has formed and the anatase phase disappears completely.

The estimated grain sizes (using Debye scherrer's formula [21]) of the TiO₂ nanofibers calcined at 400 °C, 500 °C and 600 °C were 10 nm, 16 nm and 19 nm respectively for the anatase phase whereas grain sizes of the rutile phase were of 32 nm, 49 nm, 67 nm and 78 nm for calcination temperatures 400 °C, 500 °C 600 °C and 700 °C respectively (shown in Table 1). It was concluded that the calcination temperature induces phase transformation and increases the grain sizes (shown in Figure 3).

The phase contents of fabricated TiO₂ nanofibers were calculated from the respective integrated XRD peak intensity using the following equation [22]

$$X_A(\%) = 100 / (1 + 1.265 I_R / I_A) \quad (1)$$

Where, I_A , I_R is the intensity of anatase and rutile peaks

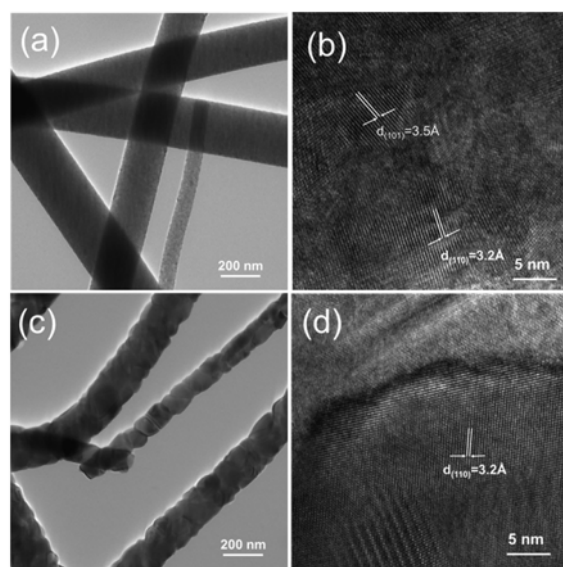


Fig. 4. Typical TEM images of TiO₂ nanofibers calcined at (a) 500 °C and (c) 700 °C, (b) HRTEM image of TiO₂ nanofibers calcined at 500 °C and (d) HRTEM image of TiO₂ nanofibers calcined at 700 °C.

respectively, and X_A is the weight percentage of anatase in the fabricated nanofibers, and the phase percentages are tabulated in Table 1. The anatase phase percentages in TiO₂ nanofibers tended to decrease after 600 °C calcination temperature; meanwhile, the rutile phase percentage increased beyond 600 °C. From these results, we may say that the rutile phase nucleated and dominated beyond a 600 °C calcination temperature.

The morphology of the calcined TiO₂ nanofibers was further studied using TEM. Figures 4(a) and 4(c) show the bright field images of 500 °C and 700 °C calcined nanofibers, respectively. It is clear from the bright field images that nanofiber diameters decrease with increasing calcining temperature, and grain sizes increase with rise in calcining temperature, which is consistent with the XRD results. Figure 4(b) and 4(d) show high resolution TEM images of the 500 °C and 700 °C calcined nanofibers, respectively. Figure 4(b) demonstrates mixed anatase ($d_{101} = 3.5$ Å) and rutile ($d_{110} = 3.2$ Å) phases of TiO₂ nanofibers, whereas Fig. 4 (d) contains only the rutile phase ($d_{110} = 3.2$ Å), which suggests that the 500 °C calcined nanofibers were composed of both anatase and rutile phases, and the 700 °C calcined nanofibers contain only rutile phase. These results were consistent with the XRD measurements.

The photocatalytic activity of fabricated TiO₂ nanofibers was determined by degradation of Methylene blue (MB) in water. A concentration change of MB solution was measured using a UV-Vis spectrophotometer. The capacity of photo generated electrons during the photocatalytic process mainly depends on the intensity of the incident photons with equivalent energy for irradiation. In present in-vestigation we have

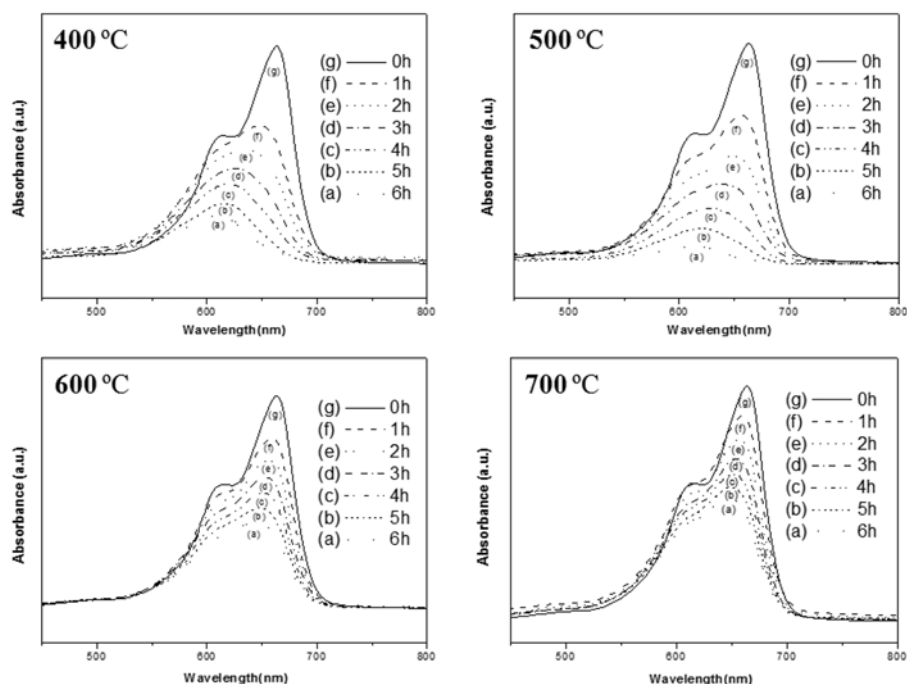


Fig. 5. Degradation of methylene blue (MB) dye using TiO_2 nanofibers calcined at (a) 400 °C, (b) 500 °C, (c) 600 °C and (d) 700 °C.

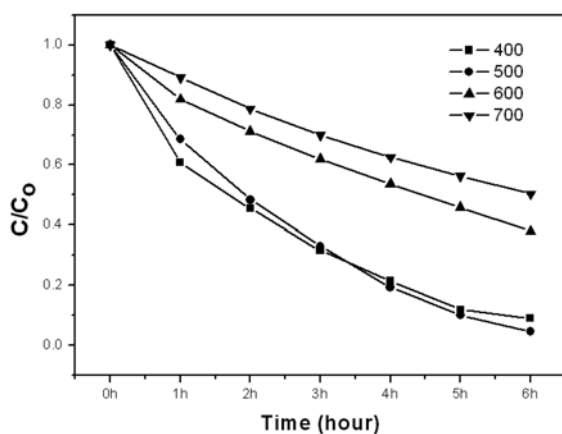


Fig. 6. Photodegradation of methylene blue (MB) by TiO_2 nanofibers (calcined at different temperatures) catalysts under UV light irradiation.

used solar light simulator for irradiation with the mixture of UV and visible light (UV : Vis = 7.8 : 92.2). Figure 5 shows absorption curves of MB solution every one hour during the photocatalysis process under solar light irradiation using TiO_2 nanofibers catalysts calcined at 400 °C, 500 °C, 600 °C and 700 °C, respectively. It is evident from the figures that the intensity of absorption maxima decreases with increasing solar irradiation time. Additionally, the absence of new absorption peaks with photocatalysis processing was observed. These manifestations showed that MB concentration decreased, and the characteristic absorption peak almost disappears, especially in Figure 5 after 6 hour solar light illumination. This shows out that 500 °C calcined TiO_2 nanofibers completely photodegraded the dye molecules.

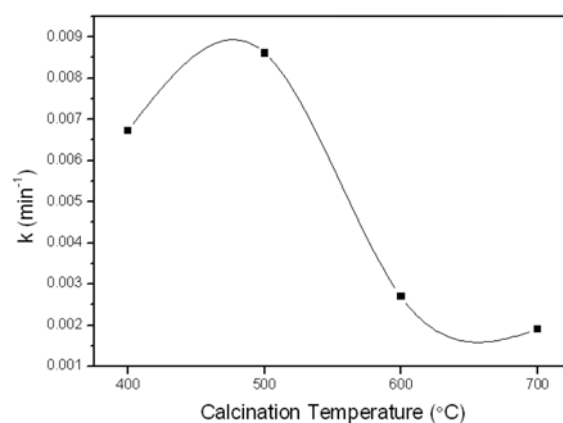


Fig. 7. Variation of degradation rate constant with calcination temperature.

Figure 6 shows the degradation of MB solution with different irradiation time, for various calcined temperatures. It is clear that with increase in calcining temperature, photocatalytic activity was enhanced. To evaluate photocatalytic efficiency, the degradation rate constant has been calculated using [8]

$$C/C_0 = e^{-kt} \quad (2)$$

Where, t is the reaction time; and C and C_0 are the final and initial concentration of MB solution, respectively. From Figure 7, it is evident that the photocatalytic efficiency is calcination temperature dependent. The presence of both anatase and rutile- TiO_2 could lead to the increase of photocatalytic activity, due to the more effective separation of electron-hole pairs [23]. TiO_2 nanofibers calcined at 500 °C show complete

degradation of MB, indicating an optimum calcination temperature. Beyond 500 °C calcination, photocatalytic activity decreased, and disappears after 700 °C.

On the basis of the preceding analysis, it is suggested that the enhanced photocatalytic activity of the 500 °C calcination nanofibers could be attributable to a favorable anatase to rutile phase ratio (76 : 24) in addition to UV and Visible light combination. This may be ascribed to the high percentage of anatase phase in nanofibers, which is considered the majority dynamic phase in photocatalytic activity, with small particle size (as evident from XRD studies), with high surface area. Moreover, 24% rutile phase in the mixed phase nanofibers enhanced the photocatalytic activity, owing to hindered charge recombination by means of electron transform from anatase phase to rutile phase at trapping states [24]. Hence, from XRD measurements and photocatalytic activity studies, a mixed phase (76 : 24) comprised of anatase and rutile phases is more preferable for photocatalysis.

Conclusions

The influence of calcination temperature on the morphology, crystalline structure and photocatalytic activity of TiO₂ nanofibers was examined and discussed. The multiphase TiO₂ nanofibers were fabricated by electrospinning and subsequent calcination of as-spun nanofibers. XRD measurements revealed that the mixed phase nature of TiO₂ nanofibers comprise of anatase and rutile phases up to 600 °C and pure rutile phase at 700 °C calcination temperatures. The polycrystalline TiO₂ nanofibers are 350-155 nm in diameter. The average grain size increased with increase in calcining temperature. The TiO₂ nanofibers calcined at 500 °C showed the highest solar light driven photocatalytic activity. It was found that the morphology, crystalline structure and photocatalytic activity of TiO₂ nanofibers strongly depended on the calcination temperature.

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