

PHOTOCATALYTIC ACTIVITY VIA SYNTHESIS OF TiO₂ NANOWIRES CONTROLLED MICROSTRUCTURE AND SURFACE AREA BY ELECTROSPINNING METHOD.

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1 Introduction

The volatile organic compounds (VOCs) with water and air pollution are widely used in industrial process and domestic activities. The VOCs are known to be toxic and considered to be carcinogenics. The most significant problem related to the emission of VOCs is generated the potential production of photochemical oxidants such as ozone and peroxyacetyl nitrate. The photocatalytic activity of the volatile organic compound is promising for purification of polluted air and water.

Since photolysis activity of photochemical water splitting over TiO₂ photoelectrode was investigated by Fujishima and Honda in 1972 [1], Many groups had been studied environmental remediation technologies using photocatalytic activity, which decomposes organic compounds by oxidation of semiconductor materials with hole (H⁺) generated in the valence band and with hydroxyl radical (OH⁻) produced by photocatalytic materials such as TiO₂, SiO₂, ZnO, CdS. Among them, Titanium dioxide (TiO₂) was generally known to one of the most popular and promising materials because of its wide band-gap, photoactivity, biocompatibility, chemical and thermal stability, and low cost. Especially, TiO₂ has a wide band gap energy (3.2 eV), which is performed to high capability of catalytic decomposition in the reaction of the generated electron and hole by absorption of photoenergy. In addition, the TiO₂ in photocatalyst activity has many advantages such as stable in various solvents under photoirradiation, available commercially from low cost, a simple process, and has strongly ability to decompose various types of redox reactions.

The photocatalytic activity of TiO₂ is largely determined by properties such as the dimension, crystalline phase, morphology, specific surface area,

and porous structure [2]. The crystalline phase is influenced surface area by crystalline size. TiO₂ with a large surface area and porous structure is expected to prevent the electron-hole recombination and increase reactant quantity onto the photocatalyst surface [3]. As the photocatalytic materials, TiO₂ nano-powders have been widely used in the photocatalytic activity. Various synthesis methods such as sol-gel, hydrothermal, and electrochemical method have been used to fabricate TiO₂ nano-powders, which were difficult to controlled uniform diameter and porous structures. In addition, TiO₂ based powders were aggregated easily by physical properties and reduced surface area by aggregation of powder [4]. For comparison, One-dimension TiO₂ nanowires, though aggregated between grains, were separated wires having sufficiently large surface area, which is expected to high photocatalytic efficiency with prevented the electron-hole recombination and increased reactant quantity onto the photocatalyst surface and the production of active oxygen species comparing to powder or bulk materials.

The parameters of process such as precursor concentration, applied voltage, viscosity lead to TiO₂ nanowires using electrospinning, which have larger surface area and high porosity compare to powder or bulk materials. In addition, electrospinning has advantages, such as simplicity of process and production of continuous nanowires with controlled diameter size from several nanometers to sub micrometers. The electrospun nanowires can be obtained calcined morphology and controlled crystalline phase by heat treatment.

Many groups [5-6] have already prepared that TiO₂ nanowires were applied to photocatalyst activity. However, most of them have rarely been

investigated that the properties of crystalline phase and crystalline size with controlled calcination temperature and specific surface area of synthesized TiO₂ nanowires using electrospinning were evaluated by the photocatalyst activity of gaseous.

In this paper, TiO₂ nanowires with large surface area and different crystalline phase were fabricated by using electrospinning process, and photocatalyst activities were studied by measuring the degradation of quantifying VOCs gas such as gaseous acetaldehyde and ammonia. In the electrospinning process, it can be easily obtained to nanowires with controlling surface area and microstructure by changing the condition such as contents of TiO₂ precursor and calcination temperature. The crystalline phase of the synthesized nanowires was controlled by heat treatment. TiO₂ nanowires were characterized by X-Ray Diffraction (XRD) for confirming the crystalline phase. The morphology of TiO₂ nanowires were observed by the FE-SEM. The surface area, porosity, and pore size distribution of TiO₂ nanowires were characterized as Brunauer-Emmett-Teller (BET).

2 Experimental

2.1 Preparation of TiO₂ nanowires

The synthesis method of TiO₂ nanowires was basically introduced as in previous work [7]. The TiO₂ sol was prepared by titanium (IV) isopropoxide (TTIP; 97%, Sigma-Aldrich) with a mixture of anhydrous ethanol (99.5+%, Sigma-Aldrich) and acetic acid (100%, Dae Jung). Next, Poly (vinylpyrrolidone) (PVP; Mw 1 300 000, Sigma-Aldrich) was dissolved in anhydrous ethanol (99.5+%, Sigma-Aldrich) and added to the TiO₂ sol solution. The precursor mixture was stirred for 10 min at room temperature and loaded into a syringe connected to a needle of 30 gauge inner diameter. A direct-current electric field was applied between the needle and collector using a high voltage. The mixture solution was fed at a rate of 0.3 ml/hr using a syringe pump. Samples were collected on aluminum foil of a drum collector. The distance between the needle tip and collector (TCD) was fixed at 10 cm. The electrospun PVP/TiO₂ composite nanowires were dried at 60 °C for 12 h. The PVP/TiO₂ nanowires were calcined in the range of 500 °C to 800 °C for 3 hr.

2.2 Characterization

The morphology of the electrospun PVP/TiO₂ composite nanowires and the calcined TiO₂ nanowires was characterized by FE-SEM (Hitachi S-4800). A measurement of 200 random wires taken from SEM image was determined average diameter and diameter distribution. The crystalline phase transformation and crystallite size of the TiO₂ nanowires were characterized by a XRD patterns using Cu K α radiation (Rigaku, D/MAX-2500/PC). The surface area and porosity of TiO₂ nanowires were measured by Brunauer-Emmett-Teller (BET, Quantachrome Autosorb-1) and calculated by Barrett-Joyner-Halenda (BJH) method from isotherm data.

2.3 Measurement of photocatalytic activity

The reactor for the decomposition of gas was used to TiO₂ photodegradation as shown in Fig. 1. The photocatalytic activities of the TiO₂ nanowires were evaluated by decompositions monitoring of acetaldehyde gas and ammonia gas. The reaction container (Tedlar Bag) contained TiO₂ nanowires and 3dm³ of gaseous were positioned under the UV light, which was irradiated using 20W Blacklight UV lamp (Sankyo, F20T10BLB, Wavelength : 365nm) with 1mW/Cm² of irradiation intensity. The concentration of decomposition of acetaldehyde gas and ammonia gas was measured by using Gastec Standard Detecting Tubes System (Gastec, Gas Sampling Pump : GV-100S, Acetaldehyde and Ammonia Detecting Tube Number : No. 92M and No. 3La)

3 Result and discussion

3.1 Morphology of TiO₂ nanowires

The PVP/TiO₂ composite nanowires were synthesized by electrospinning as shown in the Fig. 2 (A). In the previous work, we performed experiment to controlling PVP concentration and applied voltage [7]. In the electrospinning process, it is important to formation of uniform, smooth and non-bead wires. The solution viscosity and applied voltage in the electrospinning conditions had important parts in the formation of TiO₂ smooth wires. The lower and higher solution viscosity was confirmed formation of beads and increased average

nanowire diameter. In addition, the lower and higher applied voltage were related to increased average nanowire diameter and non-uniform nanowire. We fixed 11 wt% PVP solutions and 14 kV applied voltage to obtain nanowires with uniform, smooth, and non-beads. The average diameters of PVP/TiO₂ composite nanowires were found to be approximately 74 nm for 11 wt% PVP solutions and 14 kV applied voltage.

The synthesized PVP/TiO₂ nanowires were calcined at 500 - 800°C for 3hr. The average diameter of the TiO₂ nanowires was increased from 56 to 72 nm as the calcination temperature increased from 500 to 800°C in Fig. 2(B) – (E).

The average of diameter of the calcined TiO₂ nanowires was smaller than that of the PVP/TiO₂ nanowires due to the shrinkage caused by decomposition of PVP. However, as the calcined temperature was increased, the increased average diameters of TiO₂ nanowires caused grain growth and transformed crystalline phase.

3.2 Structure and specific surface area of TiO₂ nanowires

As shown in Table 1, crystalline phase, crystalline size, specific surface area, and porosity were related to the calcination temperature increased from 500 °C to 800 °C. The phase transformation from anatase to rutile of TiO₂ nanowires was occurred as the calcination temperature increased. The size of anatase crystalline calcined at 500 °C was 25 nm and increases to 28 nm at 600 °C. The anatase and rutile mixture phase of TiO₂ nanowires were observed when the calcination temperature reached at 700 °C. The two kinds of crystals were linked and the crystal lattices became interrupted in the transition area. The crystal lattices of the rutile phase were distorted, which was related to the incomplete transformation from anatase to rutile phase. Upon increasing the temperature to 500 °C, the crystalline size of TiO₂ nanowires was increased due to grain growth [8].

The calcined TiO₂ nanowires were observed to have higher specific surface area than commercial powder (P25, Degussa) in Table 1. The surface area and porosity were calculated from isotherm data by the multipoint Brunauer-Emmett-Teller (BET) method providing adsorption data in the relative pressure (P/P₀) range of 0.05 to 0.35, and the Barrett-Joyner-Halenda (BJH) method determined nitrogen adsorption and desorption volume. As the

temperature was increased, the specific surface area and porosity of TiO₂ nanowires were decreased from 95 to 69 m²/g, and 12.1 to 3.1%, respectively. P25 has a constant value of 65 m²/g surface area and 3% porosity. The specific surface area and porosity were determined owing to the transformation of the TiO₂ structure with collapse of the TiO₂ lattice and grain growth of TiO₂ crystallites, which depends on the calcination temperature

3.3 Photocatalytic activity

The photocatalytic activity of TiO₂ nanowires was evaluated by measuring the decomposition ability of VOCs gas under UV irradiation in the process of times. Fig. 3 shows the completely decomposed times of gaseous acetaldehyde (AcH) on the basis of 100 ppm in air under UV irradiation. In comparison TiO₂ nanowires calcined at different temperature, the calcined TiO₂ nanowires with anatase phase at 500 °C had the highest photodecomposition within 60min. This was due to the fact that the calcined TiO₂ nanowires at 500 °C showed better crystalline in anatase phase. The photodecomposition of TiO₂ nanowires with transformed crystalline phase at increased calcination temperatures was longer than the TiO₂ nanowires calcined at 500 °C. As the shown in Fig.3 (F), the average degradation time of TiO₂ nanowires were from 55 min to 115 min for temperature conditions from 500 °C to 800 °C, respectively. The P25 commercial powder (Degussa) was well known to have good photocatalytic activity. For comparison, the photocatalytic activity of P25 commercial powder was also tested under identical photocatalytic condition. Fig. 3 (E) and (F) shows the best rapidly degradation times and average degradation time of gaseous acetaldehyde on commercial powder photocatalyst. The average degradation time of P25 commercial powder was 120 min.

The photocatalytic degradation of gaseous ammonia was similar to photocatalytic degradation of gaseous acetaldehyde. Fig. 4 shows the photocatalytic degradation of gaseous ammonia on the basis of 100ppm using the calcined TiO₂ nanowires and commercial powder. The complete photodecomposition of TiO₂ nanowires was faster than the photodecomposition of commercial powder.

In comparison TiO₂ nanowires calcined at different temperature, the calcined TiO₂ nanowires at 500 °C were fastest photodecomposition. The best

degradation times of calcined TiO₂ nanowires with anatase phase at 500 °C and 600 °C were 4 hr in the Fig. 4 (A) and (B), respectively. The increased calcination temperature at 700 °C and 800 °C, the degradation times of TiO₂ nanowires with transformed phase from anatase to rutile were extended to 5hr and 6hr as shown in Fig. 4 (C) and (D). Fig. 4 (F) shows the comparison of average degradation times between the calcined TiO₂ nanowires at different temperature and the commercial powder. The average degradation times of TiO₂ nanowires were from 4 hr to 6 hr 30min for calcination temperature from 500 °C to 800 °C, respectively. In addition, the commercial powder was average degradation time of 7hr.

These results support that the degradation ability of VOCs gas was related to crystalline phase, size, specific surface area, and porosity of TiO₂ nanowire. As the increased calcination temperature, TiO₂ nanowires were occurred grain growth and transformation of phase from anatase to rutile, which decreased specific surface area and porosity. The crystalline size was affected band gap energy, which was inhibited recombination of hole and electron [9]. Therefore, the smaller crystalline size induced more powerful redox ability and larger band gap energy. In addition, crystalline phase and size were affected surface area and porosity. The large specific surface area was allowed more gaseous reactants to be absorbed onto the surface of photocatalyst, while high porosity was allowed rapid diffusion of gaseous during the photocatalytic reaction. The large specific surface area and high porosity can enhance the photocatalytic activities efficiency.

The calcined TiO₂ nanowires with porous structure had larger specific surface area and higher porosity than P25 commercial powder. The commercial powder with anatase-rutile phase and small crystalline size was obtained low specific surface area and porosity by aggregation of powder. The calcined TiO₂ nanowires showed a higher photocatalytic activity than P25 commercial powder owing to crystalline phase, crystalline size, specific surface area and porosity, which were strongly depended on the photocatalytic activity. Therefore, the calcined TiO₂ nanowires may be suitable for the application of photocatalyst at an industrial scale.

4 Conclusions

The PVP/TiO₂ composite nanowires have been successfully fabricated by using electrospinning conditions 11wt% PVP solutions and 14 kV applied voltage. After calcination of the electrospun PVP/TiO₂ composite nanowires at 500 °C, 600 °C, 700 °C, 800 °C for 3 h in air, the TiO₂ nanowires could be obtained and observed by FE-SEM. The crystalline phase with anatase and rutile of the TiO₂ nanowires were influenced by the calcination temperature. The crystalline size during calcinations of the TiO₂ nanowires was observed by XRD. In the BET result, the surface area and porosity decreased as calcinations temperature increased. For comparison the calcined TiO₂ nanowires observed a higher photocatalytic activity than P25 commercial powder. The calcined TiO₂ nanowires with anatase phase at 500 °C observed the highest photodecomposition.

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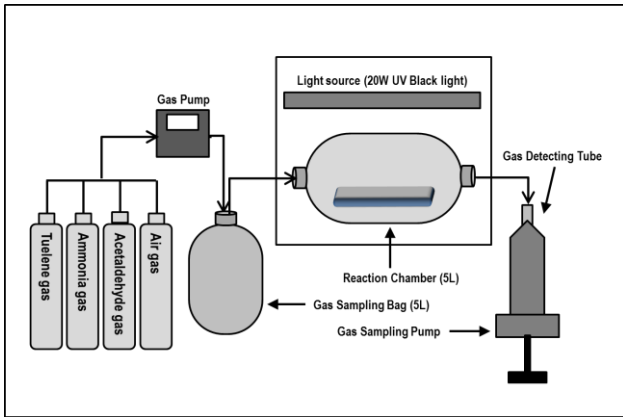


Fig. 1 Scheme of the reactor and gaseous experiment system employed for TiO₂ photodegradation

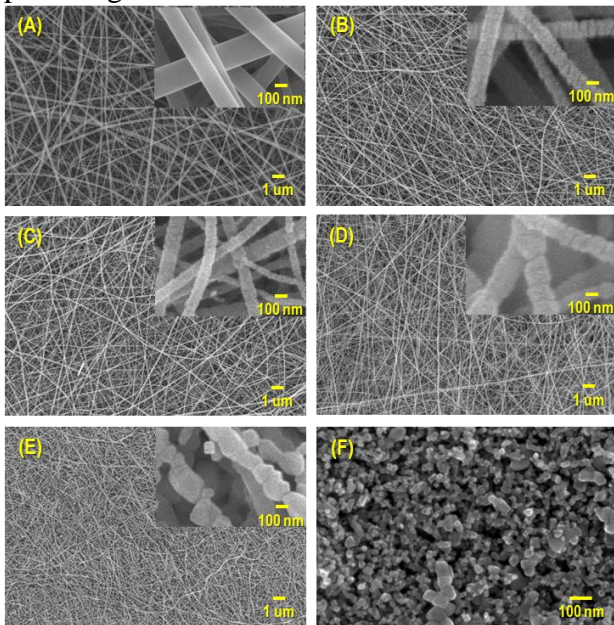


Fig. 2 FE-SEM images of (A) PVP/TiO₂ nanowires, calcined TiO₂ nanowires at (B) 500 °C, (C) 600 °C, (D) 700 °C, (E) 800 °C, and (F) P25 commercial powder

	Calcination Temperature	Crystal phase	Crystal Size	Specific Surface Area	Porosity
PVP/TiO ₂	-	-	-	-	-
TiO ₂ 500	500 °C	Anatase	25 nm	95 m ² /g	12.1 %
TiO ₂ 600	600 °C	Anatase	28 nm	81 m ² /g	7.2 %
TiO ₂ 700	700 °C	Anatase, Rutile	31 nm	78 m ² /g	7.0 %
TiO ₂ 800	800 °C	Rutile	44 nm	69 m ² /g	3.1 %
P25	-	Anatase, Rutile	30 nm	65 m ² /g	3.0 %

Table. 1 Crystalline phase, crystalline size, specific surface area, and porosity of calcined TiO₂ nanowires at various temperature and P25 commercial powder

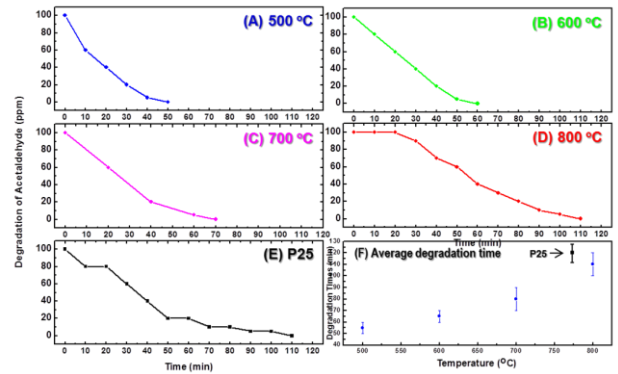


Fig. 3 Photocatalytic activity of gaseous acetaldehyde using calcined TiO₂ nanowire at (A) 500 °C, (B) 600 °C, (C) 700 °C, (D) 800 °C, and (E) P25 commercial powder and (F) average degradation times

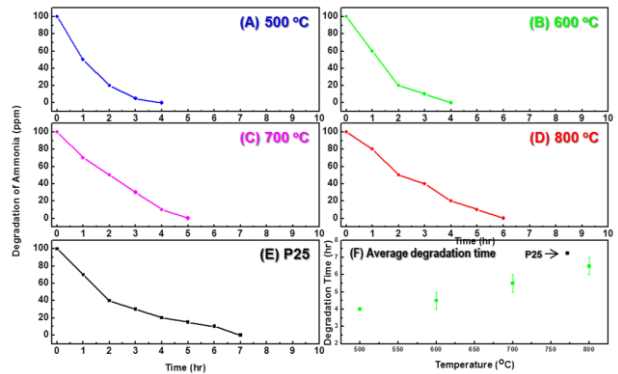


Fig. 4 Photocatalytic activity of gaseous ammonia using calcined TiO₂ nanowire at (A) 500 °C, (B) 600 °C, (C) 700 °C, (D) 800 °C, and (E) P25 commercial powder and (F) average degradation times

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