

Photocatalytic Activity for Hydrogen Evolution of Electrospun TiO₂ Nanofibers

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ABSTRACT We report herein a simple procedure for the fabrication of TiO₂ nanofibers by the combination of electrospinning and sol-gel techniques by using poly(vinylpyrrolidone) (PVP), titanium(IV) butoxide, and acetylacetone in methanol as a spinning solution. TiO₂ nanofibers (260–355 nm in diameter), with a bundle of nanofibrils (20–25 nm in diameters) aligned in the fiber direction, or particle-linked structures were obtained from the calcination of as-spun TiO₂/PVP composite fibers at temperatures ranging from 300 to 700 °C. These nanofibers were utilized as photocatalysts for hydrogen evolution. The nanofiber photocatalyst calcined at 450 °C showed the highest activity among the TiO₂ nanofibers tested such as ones prepared by the hydrothermal method and anatase nanoparticles (Ishihara ST-01). These results indicate that one-dimensional electrospun nanofibers with highly aligned bundled nanofibrils are beneficial for enhancement of the crystallinity, large surface area, and higher photocatalytic activity.

KEYWORDS: TiO₂ • electrospinning • nanofibers • hydrogen evolution • photocatalysis

INTRODUCTION

Hydrogen is recognized as an efficient fuel and an environmentally friendly gas. The production of hydrogen by direct water splitting attainable without a polluted byproduct is one of the potential alternatives to producing fuel for future energy supply (1). The water-splitting reaction over semiconductor-photocatalyst materials has attracted much attention since the first invention of photocatalytic decomposition of water into oxygen and hydrogen on photoexcited TiO₂ and at Pt counter electrodes, respectively, in 1972 (2).

Titanium dioxide (TiO₂) is one of metal oxide semiconductors that has been considerably investigated and utilized in a wide range of applications such as catalytic devices, solar cells, sensors, and other optoelectronic devices (3–7). TiO₂ is known to have three crystalline phases, i.e., anatase, rutile, and brookite. It was reported that the physical characteristics of TiO₂, including crystallization, grain size, morphology, specific surface area, surface state, and porosity, obviously influence the photocatalytic activity of TiO₂ (8–10). TiO₂ can be synthesized into various shapes, e.g., nanoporous materials, nanoparticles, nanowires, nanorods, nanotubes, and nanofibers, by different preparation methods, e.g., sol-gel, hydrothermal, solvothermal, microemulsion, and vapor deposition (11–13). Electrospinning is one of simple and versatile methods for generating TiO₂ nanofibers by combination with the sol-gel technique. The fabrication of TiO₂ nanofibers by electrospinning was first reported in 2003 (14). In particular, a solution of polymer guide and TiO₂ precursor is injected through a needle under a strong electrical field to form composite nanofibers of polymer and

amorphous TiO₂. These electrospun nanofibers can be subsequently converted into crystalline fibers via calcination (14, 15). Up to now, electrospun nanofibers have received great interest for development and utilization in some novel applications, such as chemical sensors (16), thermophotovoltaics (17), dye-sensitized solar cells (18, 19), and photocatalysts (20, 21). In our previous work, we reported the fabrication of TiO₂ nanofibers and used the obtained nanofibers as an electrode layer in highly efficient dye-sensitized solar cells with an efficiency of 8.14% with an area of 0.25 cm² (22).

For photocatalytic applications, even though successful utilizations of neat or metal-doped electrospun TiO₂ nanofibers for photooxidation of methylene blue (20) and hydrogenation of azo bonds in methyl red (21) have been reported, no prior report on the photocatalytic activities of these nanofibers for hydrogen evolution is available in the open literature. Therefore, we report herein the utilization of electrospun fibers in photocatalytic activity for hydrogen evolution.

EXPERIMENTAL SECTION

Fabrication and Characterization of TiO₂ Nanofibers. TiO₂ nanofibers were electrospun from a solution in methanol (10 mL) of 0.8 g of poly(vinylpyrrolidone) (PVP; $M_w = 1\,300\,000$, Aldrich), 4 g of titanium(IV) butoxide (TiBu; Aldrich), and 1.175 g of acetylacetone (ACA; Aldrich). ACA was used to slow down the hydrolysis and the condensation reactions for prevention of breakage of fibers during those reactions. The spinning solution was loaded into a plastic syringe, to which a 22-gauge stainless steel needle, used as the nozzle, was attached. The emitting electrode of positive polarity from a Gamma High Voltage Research power supply was connected to the nozzle, while the grounding electrode was attached to a sheet of aluminum, used as the stationary collector plate. An electrical potential of 15 kV was applied between the nozzle and the ground over a collection distance of 15 cm. The obtained fibers were left exposed to atmospheric moisture in ambient conditions for approximately 5 h to allow complete hydrolysis and

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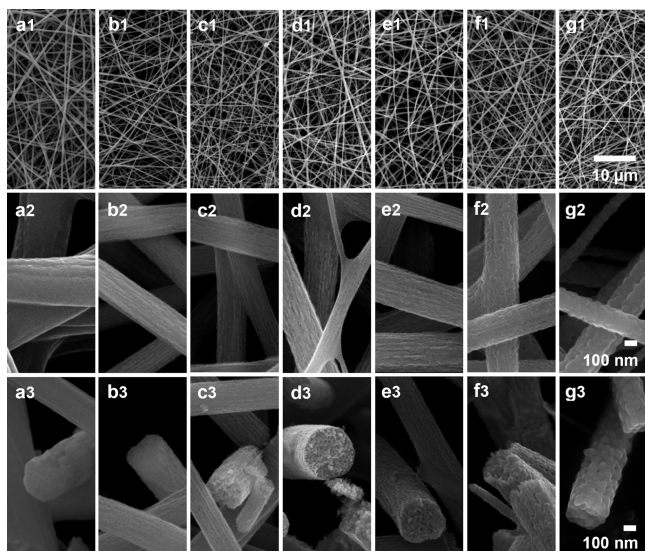


FIGURE 1. SEM images of (a) precalcined as-spun PVP/TiO₂ composite nanofibers and TiO₂ nanofibers after calcination at various temperatures of (b) 300, (c) 400, (d) 450, (e) 500, (f) 600, and (g) 700 °C for 3 h. The scale bar in figures with suffix “1” is 10 μm, while those with suffixes “2” and “3” are 100 nm. The fibers in figures with suffixes “1” and “2” are in unbroken forms, while that in suffix “3” is in broken form.

subsequently were subjected to calcination at various temperatures, i.e., 400, 450, 500, 600, and 700 °C for 3 h. The microstructure and crystalline structure of the prepared nanofibers and obtained electrode were observed and measured by using scanning electron microscopy (SEM; JEOL JSM-6500FE), transmission electron microscopy (TEM; JEOL JEM-200CT), and X-ray diffraction (XRD; Rigaku RINT 2100), respectively.

Photocatalytic Hydrogen Evolution. The photocatalytic activity of the nanofibers and nanoparticles for hydrogen evolution was investigated. One gram of sample was suspended in an aqueous methanol solution (800 mL of distilled water and 80 mL of methanol) in an inner irradiation-type photoreactor made of Pyrex glass. The mixture was purged with argon gas to remove the air dissolved in solution. A 450-W high-pressure mercury lamp (Ushio UM-452) was utilized as a light source, and cooling water was circulated through a cylindrical Pyrex jacket located around the light source to maintain the reaction temperature. The hydrogen evolved was analyzed by an online gas chromatograph (Shimadzu GC-8A, molecular sieve 5A, thermal conductivity detector, argon carrier).

Table 1. Diameters and Physical Properties of Precalcined As-Spun PVP/TiO₂ Composite Nanofibers and Calcined TiO₂ Nanofibers at Various Calcination Temperatures

material	calcination temperature (°C)	diameter of nanofibers ^a (nm)	diameter of nanofibrils or nanoparticles ^a (nm)	percentage of the anatase phase ^b	size of the anatase crystals ^c (nm)	size of the rutile crystals ^c (nm)
nanofibers	precalcined	409 ± 110				
nanofibers	300	355 ± 92				
nanofibers	400	298 ± 71	15.4 ± 3.2	100.0	13.2	
nanofibers	450	272 ± 90	20.6 ± 3.1	100.0	11.7	
nanofibers	500	261 ± 76	24.8 ± 3.7	80.3	16.1	17.4
nanofibers	600	264 ± 86	44.4 ± 5.9	7.2	25.3	30.8
nanofibers	700	259 ± 59	74.7 ± 7.2			39.9
ST-01 ^d			19.5 ± 3.3	100.0	10.4	

^a Investigated by SEM. ^b Calculated based on the procedure given by Jung and Park (24). ^c Calculated by the Scherrer equation. ^d Commercial TiO₂ powder, Ishihara ST-01, was used as-received.

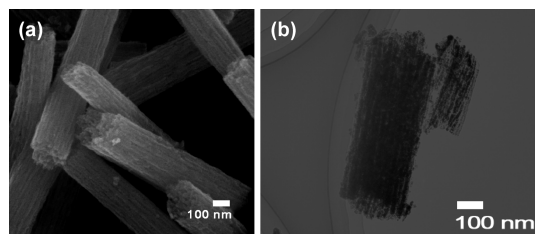


FIGURE 2. Images from (a) SEM and (b) TEM of mechanically broken TiO₂ nanofibers showing the morphology of aligned nanofibrils in the fiber direction after calcination at 450 °C.

RESULTS AND DISCUSSION

We fabricated nonwoven mats of nanofibers using the method previously developed by our group (22), which is different from other reports (14–21). Specifically, by application of a high electrical potential across a nozzle and a collector, a solution in methanol of PVP, TiBu, and ACA was electrospun to form one-dimensional (1D) continuous composite nanofibers with quite smooth surfaces and 409 nm diameter (Figure 1a and Table 1). As shown in Figure 1 (suffixes 1 and 2) and Table 1, the average diameter of as-calcined nanofibers was smaller than that of as-spun composite nanofibers. The higher the calcination temperature, the greater the shrinkage, up to a calcination temperature of 500 °C, because of the degradation of PVP and other organic contents. However, the calcination did not affect the fibrous nature of the fibers. After the heat treatment mentioned above, the average diameter of the nanofibers was found to be restrained at ca. 260 nm with a further increase of the calcination temperature from 500 to 700 °C.

Each TiO₂ fiber calcined at temperatures ranging from 400 to 500 °C is composed of a bundle of nanofibrils that are aligned in the fiber direction, as shown in Figure 1c–e. This morphology of nanofibers is shown more obviously in Figure 2 and is different from that previously reported (14, 18). This morphology indicates phase separation within the nanofibers (22). During electrospinning, the resulting fibers were exposed to atmospheric moisture so that the TiO₂ sol precursor was converted to the TiO₂ gel. Liquid–liquid phase separation results in TiO₂- and PVP-rich phases. The orientation of elongated–separated phases was formed during electrospinning and was driven by confinement and

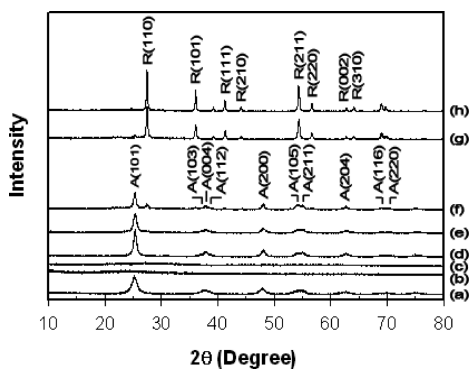


FIGURE 3. XRD patterns of (a) TiO_2 powder (Ishihara ST-01), (b) precalcined as-spun PVP/ TiO_2 composite nanofibers, and calcined TiO_2 nanofibers at various calcination temperatures of (c) 300, (d) 400, (e) 450, (f) 500, (g) 600, and (h) 700 °C with the indicated lattice planes of (A) anatase and (R) rutile phases.

the electric field (23). These separated phases were converted into nanofibrils during the calcination. The diameter of nanofibrils increased with an increase in the calcination temperature up to 500 °C. After increasing higher calcination temperatures, i.e., 600 and 700 °C, the nanofibrils are transformed to large-linked particles (Figure 1f,g) because of further crystallization and coalescence of the grains.

XRD analysis of as-spun PVP/ TiO_2 composite nanofibers revealed no evidence of a crystalline phase, although obtained composite nanofibers were subsequently subjected to calcination at 300 °C for 3 h (Figure 3b,c). Upon calcination in air at 400–450 °C, TiO_2 nanofibers were formed in the predominant content of pure anatase (Figure 3d,e). However, upon calcination up to 500 °C, anatase nanofibers formed a major crystalline phase with a slight trace of the rutile phase and the fraction of the rutile phase within the as-calcined fibers was found to increase with an increase in the calcination temperature (Figure 3f–h). On the basis of the procedure proposed by Jung and Park (24), the fractional amount of the anatase phase can be quantified, and the results are summarized in Table 1. Evidently, the fraction of the anatase phase in the as-calcined nanofibers was found to decrease with an increase in the the calcination temperature in the range of 450–700 °C.

The photocatalytic activity of the TiO_2 nanofibers for hydrogen evolution was investigated by using methanol as

a sacrificial reagent. The procedure was basically the same as that described in previous work (25). The amount of hydrogen evolved from aqueous suspensions containing differently prepared TiO_2 nanofiber photocatalysts under UV irradiation is shown in Figure 4a, while the dependence of the calcination temperature on the Brunauer–Emmett–Teller (BET) surface area and photocatalytic hydrogen evolution is depicted in Figure 4b. It should be noted that the photocatalytic activity of TiO_2 nanofibers was investigated in their raw form; i.e., the mats of the as-calcined fibers were mechanically ground and directly suspended in the reactor, without any metal dopant. A commercially available anatase TiO_2 powder (Ishihara ST-01) was also tested for comparison. No oxygen gas was detected for all experiments conducted in this study.

It was found that the photocatalytic activity increased when the calcination temperature was raised from 400 to 450 °C. In spite of the high crystallinity of the TiO_2 anatase phase of the sample calcined at 400 °C (Figure 3d), the presence of the remaining organic substance, which can cause an electron trap and/or electron–hole recombination in the sample, resulted in low photocatalytic activity. At 450 °C, the electrospun TiO_2 nanofiber photocatalyst showed the highest activity, i.e., hydrogen evolved of ca. $270 \mu\text{mol} \cdot \text{g}^{-1}$ after 5 h of irradiation of UV light (based on the amount of 1 g of catalyst), which is higher than that of the nanofiber prepared by other methods, e.g., hydrogen evolved of $95.5 \mu\text{mol} \cdot \text{g}^{-1}$ from a nanofiber prepared by the hydrothermal method (calcined at 500 °C) (25). This could be ascribed to the high crystallinity of the TiO_2 anatase phase (Figure 3e) and the high BET surface area of the sample calcined at 450 °C (Figure 4b) (25–27). In a comparison of the nanofibers prepared by electrospinning and the hydrothermal method, the BET surface areas of both samples were the same (56.3 and $58.2 \text{ m}^2 \cdot \text{g}^{-1}$, respectively) (25), while the crystallinity was different. The crystalline structure of electrospun nanofibers was 100% anatase, while that of the nanofiber prepared by the hydrothermal method was anatase and titanate B. Hydrogen evolved with electrospun nanofibers was ca. 2.8 times higher than that with nanofibers prepared by the hydrothermal method. This could be ascribed to the fact that the crystallinity of materials has much effect on the photo-

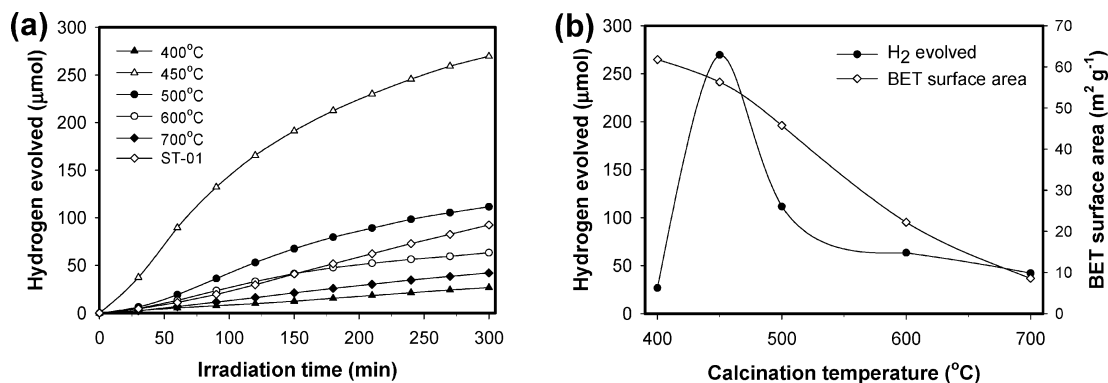


FIGURE 4. Photocatalytic activity of TiO_2 fibers for hydrogen production: (a) hydrogen production with TiO_2 fibers calcined at various temperatures, as compared with TiO_2 nanoparticle powder (Ishihara ST-01); (b) dependence of the calcination temperature on the BET surface area and photocatalytic activity of TiO_2 nanofibers for hydrogen evolution.

catalytic activity. At 500 °C, electrospun TiO₂ nanofibers showed lower photocatalytic activity because the sample showed lower crystallinity in the anatase phase when compared to the sample calcined at 450 °C and because of the presence of the rutile phase (8). This was also attributed to the lower BET surface area of the sample calcined at this temperature. A further increase of the calcination temperature resulted in lower photocatalytic activity due to a decrease in the BET surface area and an increase of the rutile phase. Furthermore, the samples calcined at 450 and 500 °C exhibited higher activity than that of commercially available TiO₂ anatase nanoparticles (Ishihara ST-01), even though ST-01 has a much higher BET surface area. In Table 1, the values show that the diameter of nanomaterials, percentage of the anatase phase, and size of the anatase crystals of nanofibers calcined at 450 °C are similar to those for nanoparticles. This could be attributed to the unique 1D structure of prepared TiO₂ nanofibers and the advantage of 1D materials (21, 25). In the case of nanoparticles, despite its large surface area, the imperfect particle and crystallinity is considered to favorably increase the probability of electron–hole recombination at both surface and bulk traps. In contrast, the use of the TiO₂ nanofibers with unique 1D structure and high crystallinity might be able to decrease the number of lattice defects and subsequently facilitate the electron transport for reaction with water molecules adsorbed at the TiO₂ surface along the 1D structure. Moreover, a reasonably high BET surface area of the 1D structure resulted in a high number of photocatalytic reaction sites.

CONCLUSIONS

We have prepared TiO₂ nanofibers by combined electrospinning and sol–gel techniques with new types of precursors in a spinning solution. TiO₂ nanofibers (260–355 nm in diameter) were obtained from calcination at temperatures ranging from 300 to 700 °C. These nanofibers were utilized in the photocatalytic activity for hydrogen evolution. The TiO₂ nanofiber photocatalyst calcined at 450 °C showed the highest activity, which is higher than that with a nanofiber prepared by other methods, e.g., hydrothermal method, and also higher than reference commercial TiO₂ nanoparticles. These results indicate that 1D electrospun nanofibers composed of well-aligned nanofibrils in the fiber direction are beneficial for the enhancement of crystallinity, the surface area, and the photocatalytic activity for hydrogen evolution. The methodology and results described in this report offer a straightforward guide to the immobilization of novel nanofiber photocatalysts for water splitting and hydrogen evolution.

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Supporting Information Available: Supplemental SEM image and XRD patterns. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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