

Visible Light Responsive Electrospun TiO₂ Fibers Embedded with WO₃ Nanoparticles

Kazuya Nakata,^{*1,2} Baoshun Liu,¹ Yuri Goto,^{1,3} Tsuyoshi Ochiai,^{1,2} Munetoshi Sakai,¹

Hideki Sakai,³ Taketoshi Murakami,¹ Masahiko Abe,^{2,3} and Akira Fujishima^{*1,2}

¹Photocatalyst Group, Kanagawa Academy of Science and Technology,

KSP Building East 412, 3-2-1 Sakado, Takatsu-ku, Kawasaki, Kanagawa 213-0012

²Research Institute for Science and Technology, Energy and Environment Photocatalyst Research Division,
Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601

³Faculty of Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510

(Received July 14, 2011; CL-110607; E-mail: pg-nakata@newkast.or.jp)

TiO₂-WO₃ composite fibers were prepared by electrospinning. The fibers have an average diameter of 1.0 μm. The XRD pattern of the TiO₂-WO₃ composite fibers indicates the presence of anatase and rutile phases of TiO₂ and an orthorhombic phase of WO₃. The photocatalytic degradation of acetaldehyde under visible light was achieved with the TiO₂-WO₃ composite fibers.

Photocatalysis based on TiO₂ is widely used for many applications such as air and water purification, self-cleaning and antibacterial surfaces.¹⁻³ A current effort in photocatalysis is the improvement of the photocatalytic performance of TiO₂, which is only able to use UV light (<400 nm) comprising 3% of the solar spectrum. Thus, it is very important to develop efficient photocatalysts that can be driven by visible light comprising about 42% of the energy of the solar spectrum. TiO₂-WO₃ composites have been shown to be efficient photocatalysts driven by visible light because of the combination of the narrow band gap of WO₃ and charge separation at the interface of TiO₂ and WO₃.⁴⁻⁷

Another approach to improve the efficiency of TiO₂ is the introduction of a micro- or nanostructure because micro- or nanostructured materials have a larger surface area and a stronger adsorption capacity, which favors photocatalytic performance. Electrospinning is a significant process because it allows for the preparation of fibers with facility and versatility.⁸⁻¹⁰ The electrospun fibers can be treated as self-standing film and have 3-D open structure, which is an advantage for photocatalytic reaction.

In this work, the preparation, characterization, and evaluation of the photocatalytic performance of a TiO₂-WO₃ composite fiber prepared by electrospinning was examined.

The preparation of the TiO₂-WO₃ composite fiber was carried out as follows: poly(vinylpyrrolidone) (PVP) was dissolved in a mixed solution containing EtOH (13 mL) and acetic acid (1.9 mL) followed by stirring for 1 h. The obtained solution was added to titanium tetraisopropoxide (6.3 mL). After further stirring for 1 h the solution was added to WO₃ particles (1.0 g, Aldrich). The as-prepared solution was loaded into a syringe and the nozzle, which was connected to a positive electrode from a high voltage generator, and a metallic plate covered with a piece of aluminum foil was used as a collecting substrate; this was grounded. The voltage was set at 15 kV and the working distance was 15 cm. The electrospun fiber was calcined at 600 °C for 2 h in air to remove the PVP and to crystallize it.

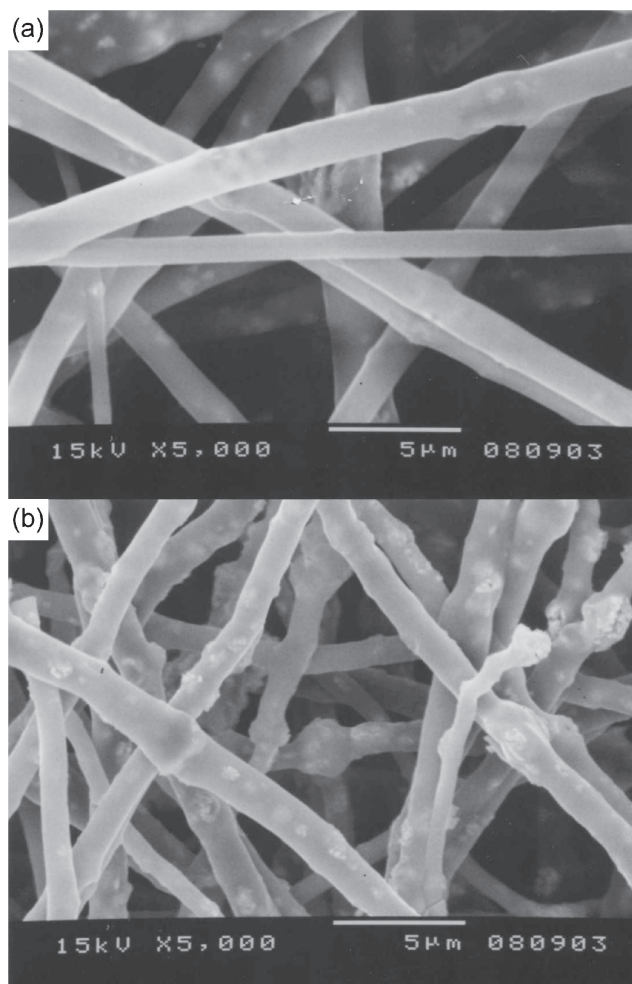


Figure 1. SEM images of the TiO₂-WO₃ composite fiber (a) before and (b) after calcination.

Figure 1 shows SEM images of the as-spun and calcined TiO₂-WO₃ composite fibers. The fibers had an average diameter of 1.2 μm before calcination. It seems that the fibers contain WO₃ particles. After the calcination the average diameters of the fibers decreased slightly (ca. 1.0 μm) because the organic component, PVP, was selectively removed by combustion and the inorganic components became crystallized.

Figure 2 shows an XRD pattern for the TiO₂-WO₃ composite fibers after calcination. The TiO₂-WO₃ composite

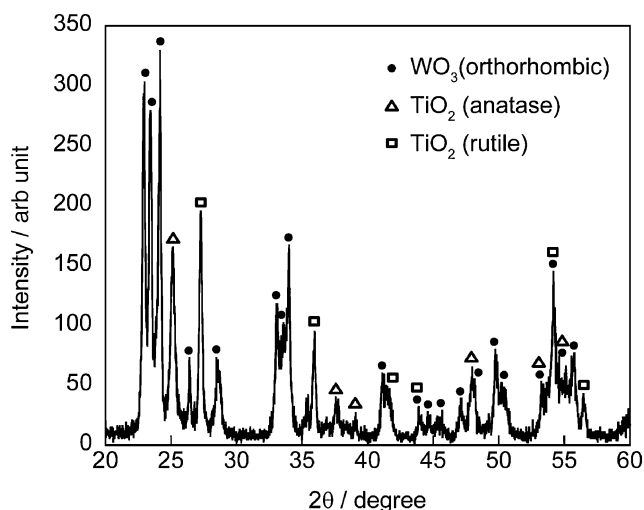


Figure 2. XRD pattern of the TiO₂-WO₃ fibers.

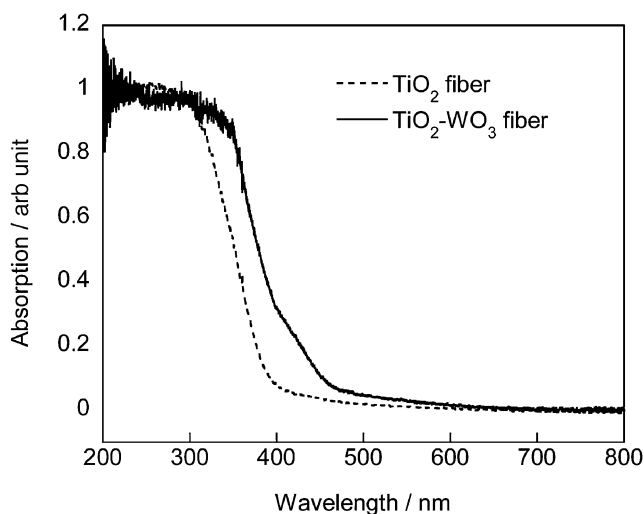


Figure 3. UV-visible absorption spectra of the TiO₂ and TiO₂-WO₃ composite fibers.

fibers contain an anatase phase and a rutile phase of TiO₂ and an orthorhombic phase of WO₃.

UV-vis spectra for the TiO₂ and TiO₂-WO₃ composite fibers are shown in Figure 3. A significant increase in the absorption at wavelengths shorter than 400 nm is assigned to the intrinsic band gap absorption of TiO₂. The absorption spectrum of the TiO₂-WO₃ composite fibers indicates the absorption of more visible light than that of pristine TiO₂ fibers, which is attributed to the fact that WO₃ has a narrow band gap.

We investigated the photocatalytic decomposition of acetaldehyde and the simultaneous production of CO₂ under visible light (>420 nm) using the TiO₂-WO₃ composite fiber after it was calcined, as shown in Figure 4. After reaching equilibrium in the dark over 1 h the concentration of acetaldehyde decreased to 70 ppm from an initial concentration of 100 ppm, and this was due to the physical adsorption of acetaldehyde on the surface of the TiO₂-WO₃ composite fiber. Upon irradiation by visible light at an intensity of 6000 lx, the concentration of the acetaldehyde decreased whereas that of CO₂ increased; its concentration

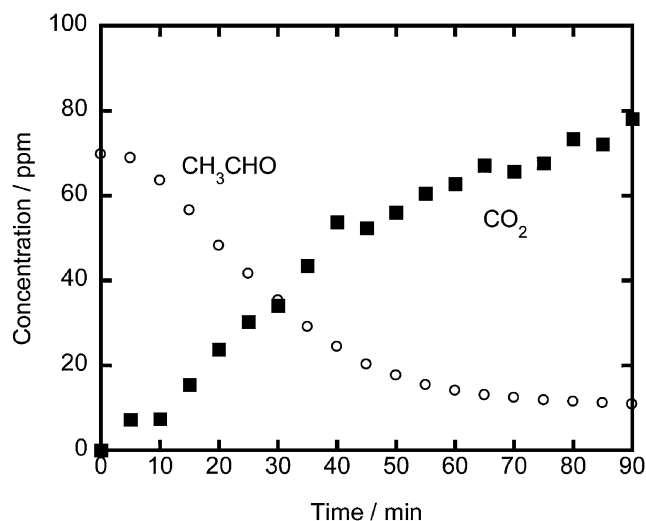


Figure 4. Photodecomposition of acetaldehyde and the production of CO₂ on the TiO₂-WO₃ composite fibers after calcination as a function of visible light irradiation time.

reached 78 ppm after 90 min. Based on the degradation reaction of acetaldehyde, the production of CO₂ will be twice (200 ppm) that of the initial concentration of acetaldehyde.⁸ In this case, the concentration of CO₂ was lower than expected for this experiment because of the generation of the intermediate product, acetic acid, during the degradation process instead of CO₂,¹¹ which is similar to the case that pristine WO₃ showed uncompleted photocatalytic degradation for acetaldehyde.¹²

In conclusion, a TiO₂-WO₃ composite fiber was prepared by electrospinning. The composite fiber shows visible light absorption. The photocatalytic degradation of acetaldehyde under visible light was achieved for the TiO₂-WO₃ composite fibers.

This work was supported by a Grant-in-Aid for Scientific Research (B) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

References

- 1 A. Fujishima, K. Hashimoto, T. Watanabe, *TiO₂ Photocatalysis: Fundamentals and Applications*, BKC, Tokyo, **1999**.
- 2 A. Fujishima, T. N. Rao, D. A. Tryk, *J. Photochem. Photobiol., C* **2000**, *1*, 1.
- 3 A. Fujishima, X. Zhang, D. A. Tryk, *Surf. Sci. Rep.* **2008**, *63*, 515.
- 4 Y. R. Do, W. Lee, K. Dwight, A. Wold, *J. Solid State Chem.* **1994**, *108*, 198.
- 5 Y. T. Kwon, K. Y. Song, W. I. Lee, G. J. Choi, Y. R. Do, *J. Catal.* **2000**, *191*, 192.
- 6 J. H. Pan, W. I. Lee, *Chem. Mater.* **2006**, *18*, 847.
- 7 K. Y. Song, M. K. Park, Y. T. Kwon, H. W. Lee, W. J. Chung, W. I. Lee, *Chem. Mater.* **2001**, *13*, 2349.
- 8 K. Nakata, N. Watanabe, Y. Yuda, D. A. Tryk, T. Ochiai, T. Murakami, Y. Koide, A. Fujishima, *J. Ceram. Soc. Jpn.* **2009**, *117*, 1203.
- 9 K. R. Reddy, K. Nakata, T. Ochiai, T. Murakami, D. A. Tryk, A. Fujishima, *J. Nanosci. Nanotechnol.* **2011**, *11*, 3692.
- 10 K. R. Reddy, K. Nakata, T. Ochiai, T. Murakami, D. A. Tryk, A. Fujishima, *J. Nanosci. Nanotechnol.* **2010**, *10*, 7951.
- 11 Z. Liu, X. Zhang, S. Nishimoto, T. Murakami, A. Fujishima, *Environ. Sci. Technol.* **2008**, *42*, 8547.
- 12 R. Abe, H. Takami, N. Murakami, B. Ohtani, *J. Am. Chem. Soc.* **2008**, *130*, 7780.