Recent Aspects of Photocatalytic Technologies for Solar Fuels, Self-Cleaning, and Environmental Cleanup

by Akira Fujishima, Kazuya Nakata, Tsuyoshi Ochiai, A. Manivannan, and Donald A. Tryk

Increasingly severe climatic, energy, and environmental problems warrant the need to continue to develop greenhouse gas-mitigating, energy-producing, energy-saving, environmentally-beneficial technologies. The closely related fields of semiconductor photoelectrochemistry and semiconductor photocatalysis, largely involving titanium dioxide, have blossomed during the past forty years since the publication of our initial work on photoelectrochemical water splitting.[1] This highly cited paper has provided a foundation for steadily increasing numbers of works on a broad range of topics, including applications such as solar light-induced water splitting (hydrogen production)[2], CO_2 reduction to produce carbonaceous solar fuels,[3] water purification, decontamination, and disinfection, as well as new materials and fundamental aspects. Our recent review summarizes a number of photocatalytic applications, including self-cleaning surfaces, anti-fogging surfaces, heat dissipation, corrosion prevention, and visible light-sensitive materials.[4] Figure 1 illustrates such a broad range of applications. The topics of "designer" titanium dioxide materials with various levels of dimensionality[5,6] and photocatalysis for environmental applications[7] have also been investigated thoroughly in our laboratory. Our early work on photocatalytic[3] and photoelectrochemical[8,9] CO_2 reduction is now continuing at present, in the laboratory of our colleague, Akihiko Kudo,[10] and in our own laboratory, both at the Tokyo University of Science, as well as by a number of other groups around the world.

At the outset, we would like to emphasize the essential unifying principles of photocatalysis before presenting some specific examples. After energetic photons are absorbed in the semiconductor, electrons and holes are generated. The mobile electrons are free to move around, reaching the surface of the solid, and then react with water or oxygen. Similarly, the mobile, highly energetic holes reach the surface and oxidize water and/or organic matter. Thus, there are four simple cases for reactions involving the electrons and holes: (Case 1) water-water, (Case 2) oxygen-water, (Case 3) water-organic, and (Case 4) oxygen-organic. Cases 3, 4, and 5 are all involved with photocatalytic decomposition of organics, whereas Case 1 is likely to be involved in the photoinduced hydrophilic effect (PIHE), as well as photocatalytic water splitting.

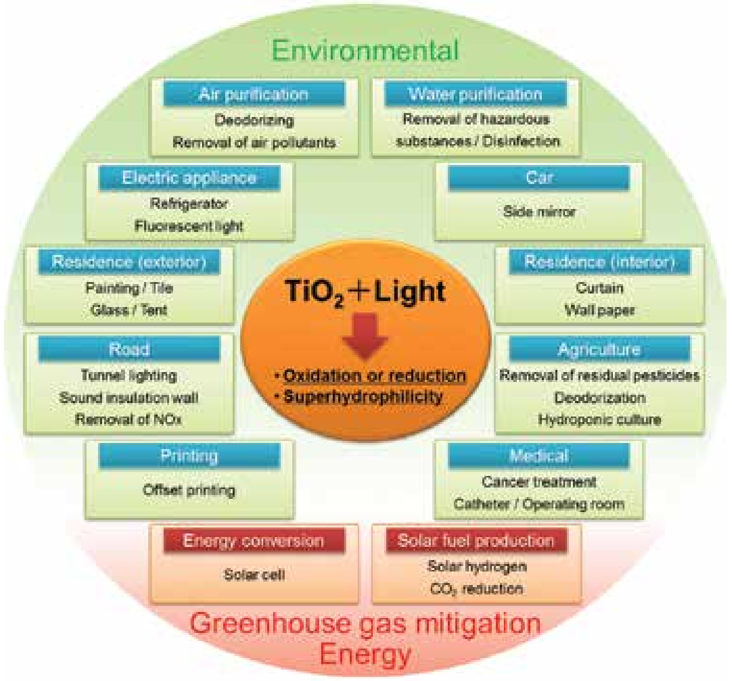

Fig. 1. *Overview of photocatalytic applications.*

These processes can be made to occur at macroscopic electrodes and thus have a strong electrochemical aspect. For example, in Case 1, the electrons are drawn off to reduce water to hydrogen at a platinum electrode, and the holes react with water at the titanium dioxide photoanode to generate molecular oxygen.[1] However, the large band gap (3.0 to 3.2 eV) of unmodified titanium dioxide made it too inefficient to produce hydrogen from sunlight due to the small number of sufficiently energetic photons. There have been several efforts to modify TiO_2 so that visible light could possibly be used. In contrast, photocatalytic cleaning can operate with fewer energetic photons, but it is still desirable to develop visible light-sensitive materials, which could be used indoors.

In this brief overview of some recent variations on the theme of photocatalysis, we describe the design of various forms of titanium dioxide with specific dimensionalities, such as zero-dimensional (0D), 1D, 2D, and 3D; and second, the development of specific environmentally-beneficial applications.

Dimensionality of Titanium Dioxide Structures

The development of new materials is strongly desired to obtain higher performance with respect to photocatalytic properties, and to find new applications for TiO_2 photocatalysis.[5] Recently, the preparation of TiO_2 nanostructures and microstructures with interesting morphologies and properties has attracted much attention, including spheres, nanorods, fibers, tubes, sheets, and interconnected architectures. Many factors, including size, specific surface area, pore volume, pore structure, crystalline phase, and the exposed surface facets, have important effects on the photocatalytic performance; thus the improvement of performance by adjusting these factors is still a major focus of photocatalysis research. Another factor that significantly affects the photocatalytic performance of TiO_2 materials is the structural dimensionality. Therefore, materials with appropriate dimensionalities enable us to take full advantage of the unique properties of TiO_2 (Fig. 2).

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Zero-dimensional nanostructured or microstructured TiO_2 spheres are the most widely studied and used TiO_2-related materials.[11,12] Such structures usually possess high specific surface area, high pore volume and pore size, high activity, and low density. All of these properties increase the accessible surface area and mass transfer for organic pollutant adsorption, resulting in better photocatalytic performance, since photocatalytic reactions are based on chemical reactions on surfaces. In 0D TiO_2 materials, *i.e.*, spheres, the introduction of both a hierarchical structure and high-energy (001) facets offer high photocatalytic activity. Recently, we reported mesoporous core–shell spheres composed of small TiO_2 nanocrystals with exposed step-like (001) and (010) facets, prepared by a method that combines electrospraying and hydrothermal treatments.[11]

Electrospraying is a technique using a high-voltage electric field to obtain microsize or nanosize spheres. In this case, core–shell TiO_2 spheres are produced by electrospraying titanium alkoxide with polyvinylpyrrolidone (PVP)(Fig. 3a). Further, hydrothermal treatment provides a hierarchical structure with tunable pore size, pore volume, specific surface area, and percentage of specified crystal facets, because PVP forms a network, and the amorphous TiO_2 particles fill the pores within the network during electrospraying of the core–shell TiO_2 spheres. Later, PVP is removed from the TiO_2 spheres (Fig. 3a), and TiO_2 is crystallized during the hydrothermal process. The crystal morphology depends on conditions such as the amount of PVP used and the hydrothermal method.

Electrospinning can also tailor TiO_2 materials with 1D structures, such as fibers and tubes, having unique properties and advantages for photocatalytic reactions. A co-jetting method has been reported for making hollow TiO_2 fibers. By using a multi-channel nozzle, multi-channel hollow TiO_2 fibers with zero to three channels can be obtained (Fig. 3b).[13] The photocatalytic performance improves as the number of channels increases, which leads to the specific surface area increase with increasing numbers of channels, and therefore multiple reflections of incident light can be expected.

The idea of 1D materials, which can decrease recombination of electrons and holes, has been combined with that of visible light absorption.[14] Nitrogen doping was found to induce visible-light-responsive photocatalytic activity but lowered the UV-light-responsive photocatalytic activity. Visible-light photocatalytic activity was concluded to originate from N 2p levels near the valence band. This work on titania nanobelts has recently been extended.[15]

As a 2D material the nanosheet is a nanosized flake with a flat surface and high aspect ratio with an extremely small thickness (1-10 nm). The platelet size could range from submicrometers to several tens of micrometers. We reported the production of a self-cleaning glass using TiO_2 nanosheets.[16] The TiO_2 nanosheets have low turbidity, strong adhesion to glass, and high hardness (Fig. 4). Furthermore, after dip-coating the self-cleaning glass in a solution containing methylene blue, very little of this dye remained on the self-cleaning glass, indicating high anti-fouling properties. This is in contrast to the case of glass coated with TiO_2 nanoparticles, which retained a significant amount of methylene blue. These results are due to the fact that the self-cleaning glass prepared using TiO_2 nanosheets has a very smooth surface, which reduces the attachment of methylene blue molecules, whereas glass prepared using TiO_2 particles has a relatively rough surface, which promotes the attachment of methylene blue molecules. Materials with this combination of low adhesion and photocatalytic properties are good candidates for new self-cleaning coatings.

Among the various morphological structures, 3D interconnected arrangements have the potential for producing a new class of materials and applications. They are important for practical applications, because 3D hierarchical structures with pores have potentially large surface-to-volume ratios, which are an advantage for effective diffusion pathways for guest species, such as organic pollutants, into the framework; this should support efficient purification, separation, and storage. Furthermore, an interconnected structure is potentially superior from a practical point of view. For example, at present, almost all photocatalytic purifiers utilize TiO_2 particles coated on porous structured ceramics; however, TiO_2 particles may be stripped from the ceramic, leading to the release of small dust particles and degradation of the photocatalytic properties. To solve such problems, self-supported porous TiO_2 frameworks, i.e., monolithic materials, are suitable candidates for water remediation.

Recently, we prepared TiO_2 monoliths and evaluated their photocatalytic performance using methylene blue decolorization. TiO_2 monoliths have a porous, interconnected structure, which is advantageous for photocatalytic decolorization. Furthermore, TiO_2 monoliths have a porous structure after calcination at high temperature with sufficiently high hardness. The combination of porous structure and hardness provide benefits for water remediation. In actuality, TiO_2 monoliths showed good performance for the photocatalytic decolorization of methylene blue. TiO_2 monoliths should realize both hardness and high photocatalytic performance for water remediation.

The dimensionality of the TiO_2 structure affects various properties such as photocatalytic performance, specific surface area, adsorption properties, reflectance, adhesion, and carrier transportation. TiO_2 is the most widely studied photocatalyst, and it is used in numerous applications because of its compatibility with modern technology. Novel forms of materials can help to develop advanced TiO_2 photocatalysts, which will improve our lives in terms of advanced energy production and environmental protection.

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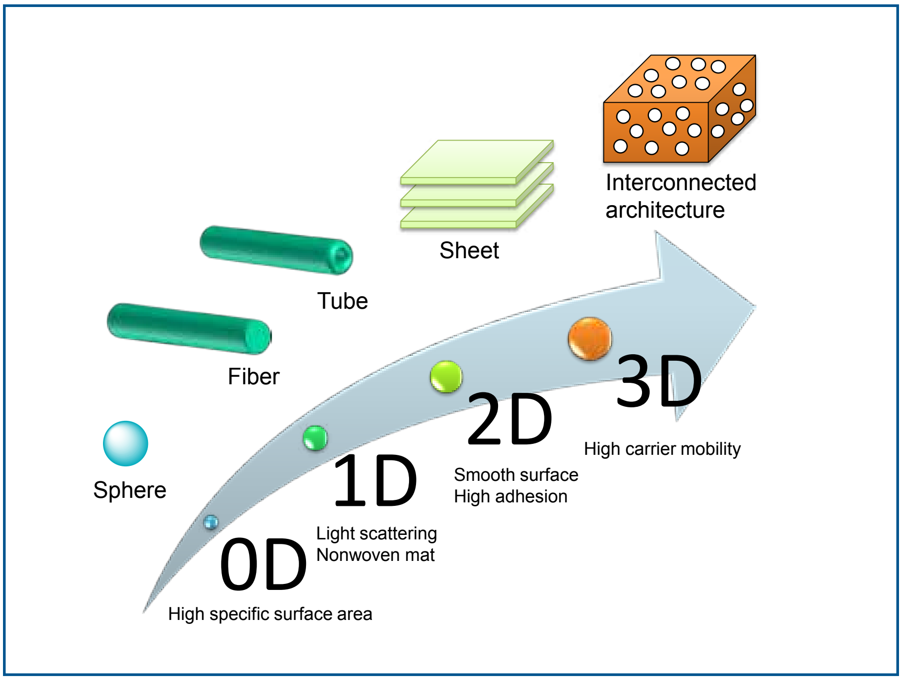

Fig. 2. *Schematic illustration of structural dimensionality of materials with expected properties.*

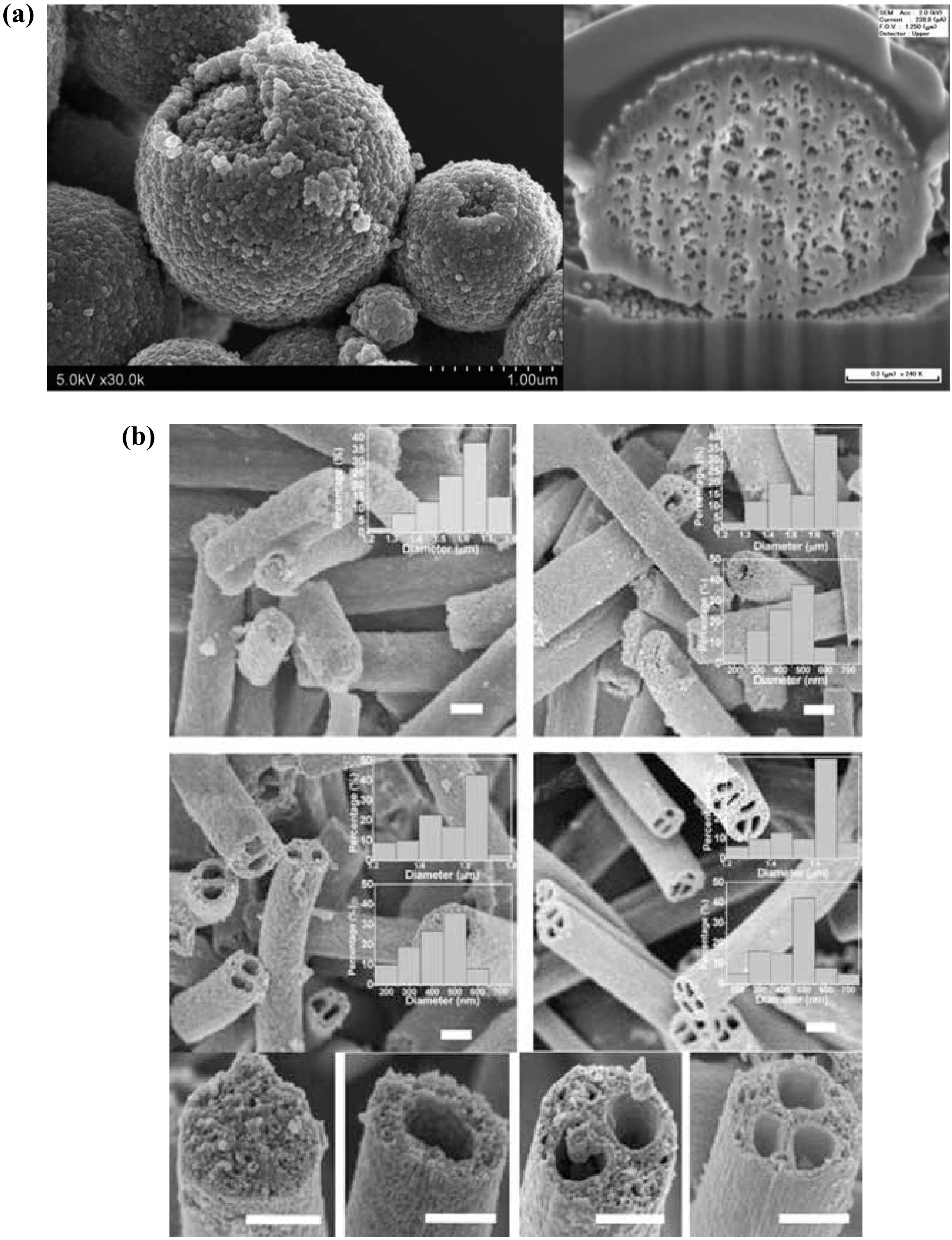

Fig. 3. *(a) FE-SEM image of zero-dimensional core-shell* TiO_2 *spheres and SEM image of cut* TiO_2 *spheres; (b) SEM images of multi-channel* TiO_2 *fibers.*

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Environmental Purification

Environmental purification, especially of indoor air and polluted water, is highly important for human life. The market for photocatalytic technology in Japan has experienced encouraging growth, approximately doubling during the last ten years, reaching on the order 1 billion USD (these data represent the sales volume for companies that are members of the Photocatalysis Industry Association of Japan). Recently, the sales volume of "cleanup" applications has increased greatly. This trend indicates the increasing numbers of people who are interested in environmental issues. For example, the swine influenza outbreak of 2009 raised serious fears of global pandemic and suddenly increased the sales volume of photocatalytic air-purifiers. The key scientific and technical requirements for effective photocatalytic environmental purification are (1) catalyst immobilization strategies, (2) integrated or coupled systems for enhanced photo-oxidation, and (3) effective design of photocatalytic reactor systems.[17]

To meet these requirements, we have fabricated a Ti-mesh impregnated photocatalyst, (TMiP®) by use of anodizing and etching methods.[18] The method used to fabricate TMiPs is shown in Fig. 5. We have found several advantages of TMiPs and their usefulness for environmental purification. The high mechanical flexibility of TMiPs allows us to design any geometry of modules for environmental purification through the combination of UV-sources and the other technologies. Our contribution in photocatalytic environmental purification with TMiPs is summarized in a recently published review article.[7] Now, we are focusing on the fabrication of practical environmental purifiers.

One of the recent applications of TMiPs is a photocatalytic-plasma synergistic air-purifier.[19] The purifier consists of two essential technologies, a plasma-assisted catalytic technology (PACT) reactor, and the TMiP, to realize the plasma-enhanced photocatalysis. A practical test for the deodorization of tobacco smoke was proposed for a life-sized smoking room (2.7 × 3.6 × 2.5 m), which included the analysis of selected gaseous pyrolytic and oxidative decomposition products by using a single-pass system from the smoking room to a non-smoking room. The amounts of all of the contaminants except acetaldehyde were significantly decreased at the air outlet of the air-purifier. Finally, the amounts of these compounds were maintained at low levels in the non-smoking room. This result indicates that nearly all of the compounds can be decomposed and/or removed by the practical single-pass air-purifier.

The continuous improvement of the material properties and the reactor design would greatly aid the creation of effective environmental purification systems. Thus, it is becoming apparent that photocatalysis has been realized as an important field of study for a healthy, comfortable living environment.

Photocatalytic CO_2 Reduction

Several years after our initial work on solar hydrogen production in the late 1960s and early 1970s, the topic of photocatalytic CO_2 reduction was taken up, an idea that was essentially unknown at that time.[3] Subsequently, the idea caught on, and several groups became interested (see Ref. 10). We also experimented with a photoelectrochemical approach, making use of high-pressure CO_2 at a p-type indium phosphide photocathode in methanol.[8,9] Recently, the photocatalytic approach has enjoyed a renewed popularity in Japan. One very recent example is the work of Kudo and coworkers, who have examined $ALa_4Ti_4O_{15}$ (A = Ca, Sr, and Ba) photocatalysts with layered perovskite structures.[10] The photocatalytic approach has also become popular in other parts of the world, for example, at the University of Nevada, in collaborative work with one of the present authors (AM).[20] Grimes and coworkers have recently published a review on solar fuel production.[21]

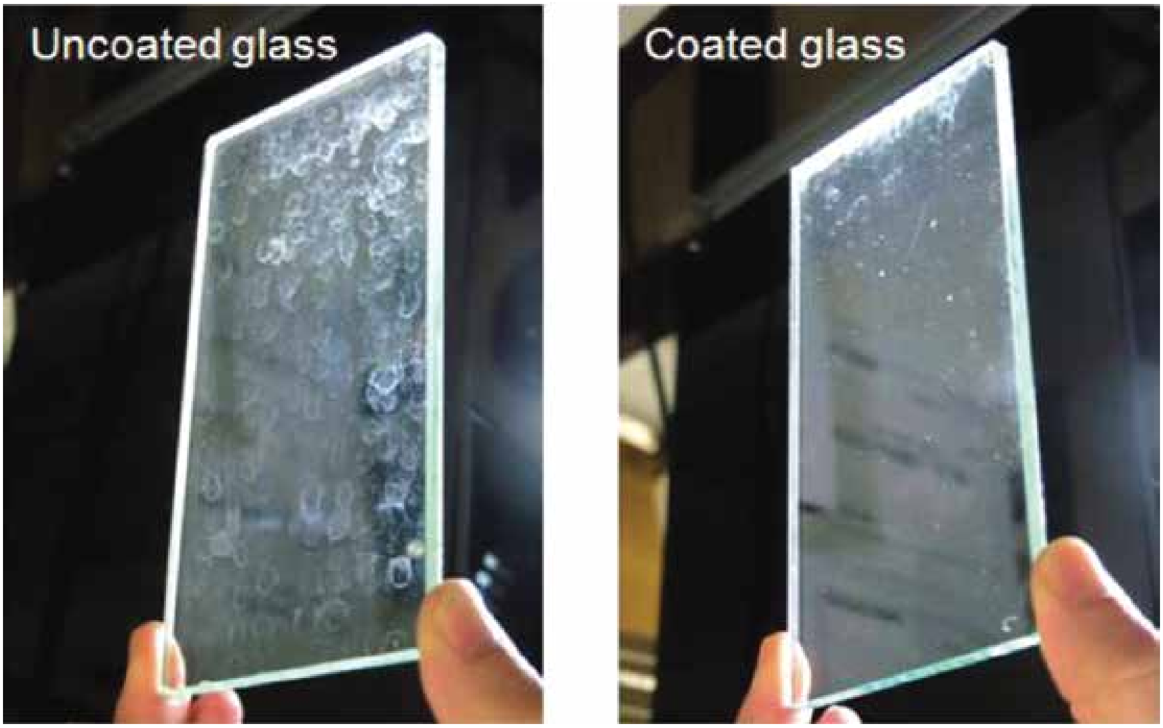

Fig. 4. *Photographs of the samples of glass coated (right) or not coated (left) with niobia nanosheets after a self-cleaning test.*

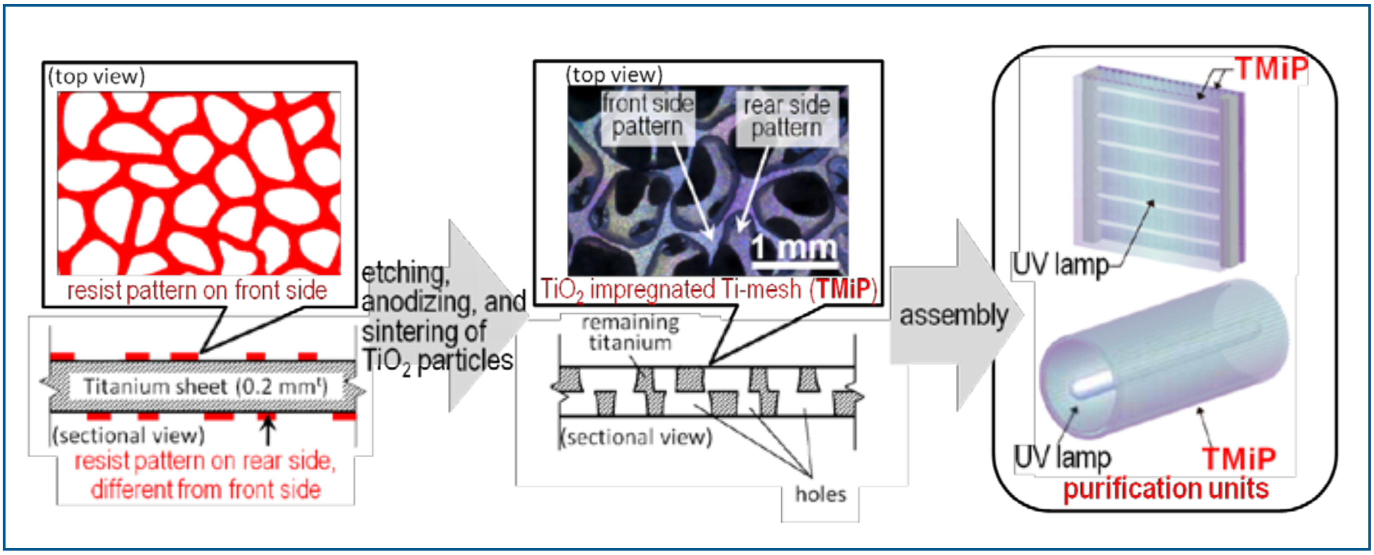

Fig. 5. *Fabrication method of TMiP.*[18]

Concluding Remarks

The work surveyed here hopefully underlines the fact that the closely-related photocatalytic and photoelectrochemical approaches are extremely versatile and can be used in numerous ways to both produce fuels and chemicals from sunlight and to carry out various light-induced self-cleaning and environmental purification functions.

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References

1. A. Fujishima and K. Honda, *Nature*, **238**, 37 (1972).
2. A. Fujishima, K. Kohayakawa, and K. Honda, *J. Electrochem. Soc.*, **122**, 1487 (1975).
3. T. Inoue, A. Fujishima, S. Konishi, and K. Honda, *Nature*, **277**, 637 (1979).
4. A. Fujishima, X. Zhang, and D. A. Tryk, *Surface Science Reports*, **63**, 515 (2008).

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5. K. Nakata and A. Fujishima, *J. Photochemistry and Photobiology C: Photochemistry Reviews*, **13**, 169 (2012).
6. K. Nakata, T. Ochiai, T. Murakami and A. Fujishima, *Electrochim. Acta,* **84**, 103 (2012).
7. T. Ochiai and A. Fujishima, *J. Photochemistry and Photobiology C: Photochemistry Reviews*, **13**, 247 (2012).
8. K. Hirota, D. A. Tryk, T. Yamamoto, K. Hashimoto, M. Okawa, and A. Fujishima, *J. Phys. Chem. B*, **102**, 9834 (1998).
9. K. Hirota, D. A. Tryk, K. Hashimoto, M. Okawa, and A. Fujishima, *J. Electrochem. Soc.*, **145**, L82 (1998).
10. K. Iizuka, T. Wato, Y. Miseki, K. Saito, and A. Kudo, *J. Am. Chem. Soc.*, **133**, 20863 (2011).
11. K. Nakata, M. Sakai, T. Ochiai, T. Murakami, K. Takagi, and A. Fujishima, *Langmuir*, **27**, 3275 (2011).
12. B. Liu, K. Nakata, M. Sakai, H. Saito, T. Ochiai, T. Murakami, K. Takagi, and A. Fujishima, *Catalysis Science & Technology*, **2**, 1933 (2012).
13. T. Zhao, Z. Liu, K. Nakata, S. Nishimoto, T. Murakami, Y. Zhao, L. Jiang, and A. Fujishima, *J. Mater. Chem.*, **20**, 5095 (2010).
14. J. Wang, D. N. Tafen, J. P. Lewis, Z. Hong, A. Manivannan, M. Zhi, M. Li, and N. Wu, *J. Am. Chem. Soc.*, **131**, 12290 (2009).
15. N. Wu, J. Wang, D. N. Tafen, H. Wang, J.-G. Zheng, J. P. Lewis, X. Liu, S. S. Leonard, and A. Manivannan, *J. Amer. Chem. Soc.*, **132**, 6679 (2010).
16. T. Shichi and K.-i. Katsumata, *J. Surface Finishing Soc. Japan*, **61**, 30 (2010).
17. M. N. Chong, B. Jin, C. W. K. Chow, and C. Saint, *Water Research*, **44**, 2997 (2010).
18. T. Ochiai, T. Hoshi, H. Slimen, K. Nakata, T. Murakami, H. Tatejima, Y. Koide, A. Houas, T. Horie, Y. Morito, and A. Fujishima, *Catalysis Science & Technology*, **1**, 1324 (2011).
19. T. Ochiai, Y. Hayashi, M. Ito, K. Nakata, T. Murakami, Y. Morito, and A. Fujishima, *Chem. Eng. J.*, **209**, 313 (2012).
20. K. S. Raja, Y. R. Smith, N. Kondamudi, A. Manivannan, M. Misra, and V. Subramanian, *Electrochem. Solid-State Lett.*, **14**, F5 (2011).
21. S. C. Roy, O. K. Varghese, M. Paulose, and C. A. Grimes, *ACS Nano*, **4**, 1259 (2010).

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