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Preparation of a TiO_2 based multiple layer thin film photocatalyst

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A TiO_2 thin film semiconductor is expected to show high photocatalytic activity because of the short diffusion distances of photoexcited electrons and holes to the surface as well as the short spatial separation of reducing and oxidizing sites. The multiple layer photocatalyst, reported herein, which consists of a TiO_2 thin film, platinum electrode and porous alumina substrate, was prepared by spin-coating a TiO_2 sol and sputter-coating of a platinum electrode on a porous substrate. After adequate heat treatment, this multi-layered photocatalyst showed a high efficiency for H_2 generation from ethanol aqueous solution under UV illumination as compared with platinized TiO_2 fine particles.

Research into photocatalytic reactions mediated by metal oxide semiconductors received a further boost after the work of Fujishima and Honda on the photoelectrolysis of H_2O using TiO_2 electrodes.[1] Since that study was reported, a considerable amount of work involving metal oxide semiconductor photocatalysts has been done. To date, no substance superior to TiO_2, however, has been found. TiO_2 is especially attractive because of its high photocatalytic activity and chemical stability in aqueous solution under light irradiation. Recently, two branches involving the study of the TiO_2 photocatalyst have emerged especially for the purposes of solving environmental issues. One branch involves the use of highly dispersed fine particles in a porous material,[2–4] and the other is concerned with TiO_2 thin films.[5–10]

Most TiO_2 thin films are prepared by coating a substrate with a TiO_2 sol, thereby producing a thin film consisting of TiO_2 particles. Generally, this methodology often results in a porous TiO_2 film. The fine particles that make up the film have several advantages, for example, large specific surface areas, short diffusion distance to the surface for the photo-generated electrons and holes, and quantum size effects for particles of <10 nm in diameter.[11] However, some disadvantages of fine particles include problems associated with the close proximity of the redox sites due to small particle sizes, *i.e.*, the progress of reverse reactions between the products (oxidants and reductants) on the surfaces of particles is hard to inhibit.

Nonetheless, an attractive photocatalytic system for spatially separating the respective oxidation and reduction sites is an unsupported thin film system consisting of a semiconductor and an appropriate metal electrode. This system is also expected to minimize diffusion distances to the surface for the photogenerated charge carriers. The fabrication of such a thin film system on the nanometer or mesoscopic scale is obviously very challenging. There are some reports on TiO_2 thin film photocatalysts supported on metal electrodes[12–14] or on porous substrate.[15] However, it is not clear whether these photocatalytic systems were intended to spatially separate photogenerated electrons and holes or not.

In this work, a photocatalyst comprising a TiO_2 thin film and platinum electrode was fabricated on a silica gel coated porous alumina substrate as schematically illustrated in Fig. 1. In this multiple layer system, UV light irradiation is expected to induce the following redox reaction; oxidation on the surface of the TiO_2 thin film and reduction on the metal electrode. For the reduction reaction, the oxidant is expected to migrate to the platinum electrode surface *via* the porous substrate and porous silica gel layer.

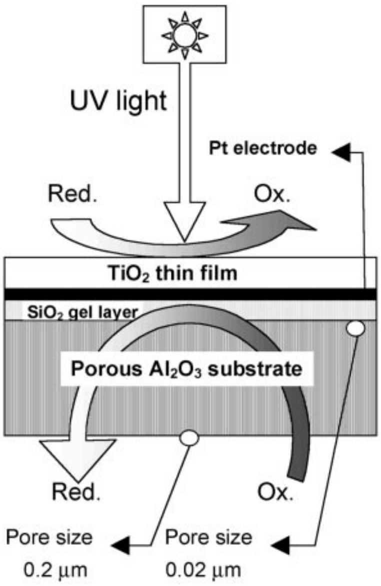

Fig. 1 Schematic illustration of a TiO_2 based multiple layer thin film photocatalyst.

Experimental

The TiO_2 thin film was prepared by a sol–gel method. The flowchart for the preparation of the TiO_2 sol precursor is shown in Fig. 2. This procedure was adapted from the method reported by Sakka and Kamiya.[16] Reagent grade titanium tetraisopropoxide (3.98 g, TTIP, Wako Pure Chemicals) was stabilized with 0.33 ml of acetylacetone (AcAc, Wako) and 130 ml of isopropanol (Pr^iOH, Wako). Stabilization of TTIP ensures that during hydrolysis only isopropoxyl groups are removed, and consequently this prevents the rapid growth of the TiO_2 particles. Stabilized TTIP was hydrolyzed with 0.98 g of acetic acid (Wako), 0.76 ml of distilled water and 10 ml of Pr^iOH under an argon atmosphere resulting in a transparent yellowish TiO_2 sol. The molar ratio of TTIP : AcAc : H_2O was 1 : 0.23 : 3. The particle sizes in the TiO_2 sol were <10 nm in diameter as observed by transmission electron microscopy.

A flowchart for the fabrication of the thin film photocatalyst is shown in Fig. 3. An alumina membrane filter (Whatman, Anodisk 25) was used as the porous substrate. This filter is *ca.* 60 µm in thickness and has an asymmetric pore structure with pores of diameter of 0.02 µm and 0.2 µm. The surface of

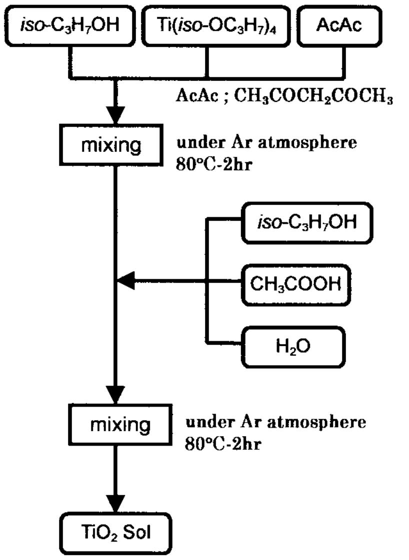

Fig. 2 Flowchart of the preparation of the TiO_2 sol.

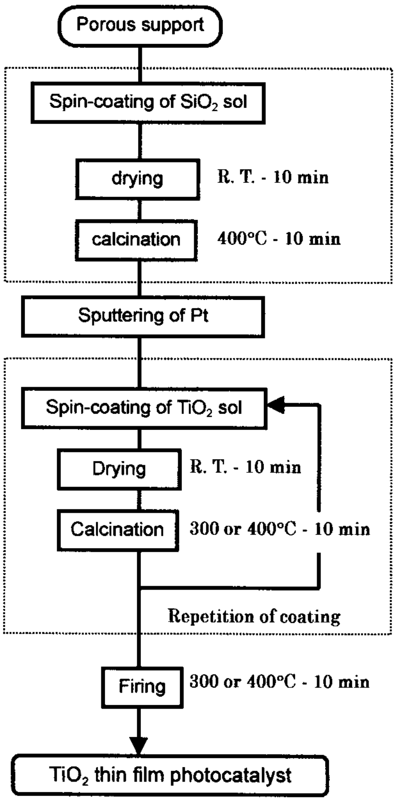

Fig. 3 Flowchart for the fabrication of the TiO_2 thin film photocatalyst.

the porous substrate was coated with a silica sol (Nissan Chemical, Snowtex N) in order to make the surface smooth thereby preventing the Pt and TiO_2 fine particles from going through the substrate. This silica sol contains 20–21 wt.% of silica and the colloidal particles are 10–20 nm in diameter. The sol was diluted to 10 vol% with reagent grade ethanol and the coating was made just once a low speed spin coater (Thomas TM-701, *ca.* 300 rpm). After drying at 60 °C and calcining at 300 °C, platinum was sputter-coated on the silica gel layer. The platinum surface was subsequently coated with the TiO_2 sol, dried at 60 °C for 10 min and calcined at 300 °C for 10 min. This coating procedure for the TiO_2 sol was repeated until the desired film thickness was obtained. Finally, the sample was heat-treated at a selected temperature in the range 300 to 700 °C.

The surface and the cross-section of the thin film were observed by scanning electron microscopy (Hitachi S-2050 SEM and JEOL JCM-890S FE-SEM). In order to evaluate the thickness of the TiO_2 layer, the TiO_2 layer was distinguished from the platinum and silica layers by both secondary electron image (SEI) and back scattered electron image (BEI) observations of the sample cross section. Crystalline phases of the samples were identified by X-ray diffractometry (Rigaku Geigerflex System, Cu-Kα radiation).

The photocatalytic activity of the sample was evaluated by measuring the photogeneration rate of hydrogen from an aqueous solution of ethanol. The simplified model of the photoredox system in an aqueous solution of ethanol mediated by the multilayered photocatalyst is also shown in Fig. 1. Ethanol is oxidized to acetaldehyde, acetic acid or CO_2.[17] Protons are reduced to hydrogen molecules on the platinum electrode. The photocatalyst was immersed in 500 ml of a 20 vol% aqueous ethanol solution under an Ar atmosphere. Illumination of the photocatalyst (TiO_2 film side) was carried out using a 300 W Xe lamp (ILC Tech., LX300F). A water cell was used as an infrared filter. The photogenerated hydrogen was detected by gas chromatography (Shimazu GC-6A with a thermal conductivity (TCD) cell and a 2 m long molecular sieve 5A column). Argon was used as the carrier gas. A platinized commercial TiO_2 powder (Nihon Aerosil P-25, anatase, particle diameter 10–50 nm) was used as a reference sample. Platinization of the powder was carried out by a photodeposition method in an H_2PtCl_6 aqueous ethanol solution.[2]

Results and discussion

The XRD patterns of as-prepared samples showed only a halo indicating that the TiO_2 layer was amorphous. Upon heat-treatment at >300 °C for 4 h, a diffraction peak corresponding to the (101) plane of anatase appeared on the pattern and the crystalline phase of all heat-treated samples was predominantly anatase. The anatase crystallites were highly oriented along the (101) plane. The crystallite size was calculated by Sherrer's equation assuming that there was no distortion in the crystal. As the temperature of heat treatment was increased, there was a parallel gradual increase in the peak intensities and crystallite size of anatase from *ca.* 10 nm (at 330 °C) to *ca.* 15 nm (at 500 °C).

SEM images revealed that the surface (TiO_2 film side) of the sample fired at 450 °C was devoid of any surface texture, *i.e.*, it was very smooth and flat. Images of the cross section of this sample are shown in Fig. 4. The two SEI images show the pore structures of the alumina substrate and the overlayers. In the BEI image, the bright part was identified as the platinum layer. Clearly these images exhibit the expected structure of the multi-layered thin film system. We estimated the thickness of the TiO_2 layer in all samples from the SEI + BEI image. The change of TiO_2 film thickness with the number of coating applications is shown in Fig. 5. It is apparent that film thickness increased in proportion to the number of coating applications. Each coating application produced a film about 10 nm thick. This film thickness corresponds to the crystallite size as estimated from the XRD measurement. This shows that the TiO_2 sol particles maintained their dispersive condition, with the subsequent production of a dense and flat TiO_2 thin film.

The photocatalytic activity of the photocatalyst was evaluated by monitoring the rate of hydrogen evolution from an aqueous ethanol solution as already outlined in the Experimental section. The hydrogen generation rate per unit surface area for the eight-coated sample as a function of firing temperature is shown in Fig. 6. The rate increased fairly steeply up to 400 °C and decreased gradually thereafter. The increase

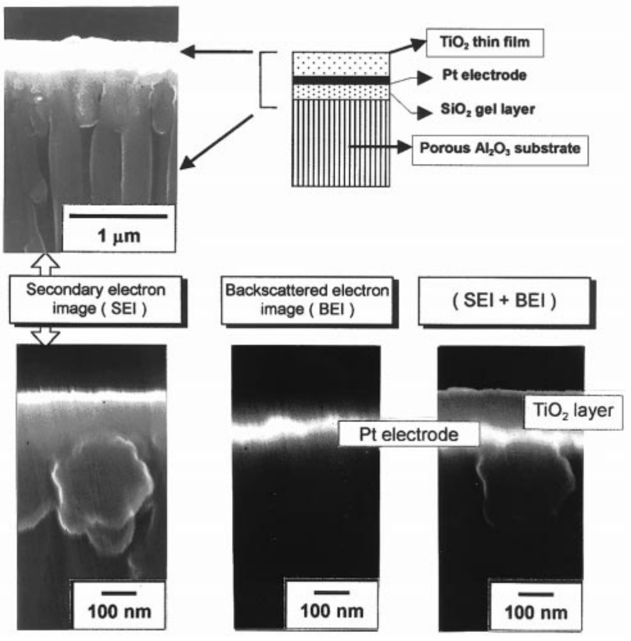

Fig. 4 SEM images of the cross-section of the TiO_2 thin film photocatalyst.

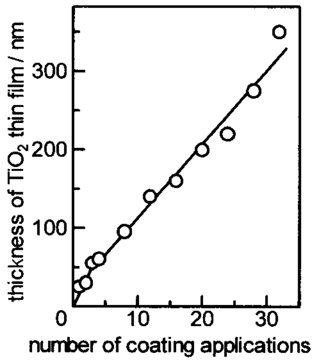

Fig. 5 Change of the TiO_2 film thickness with the number of coating applications.

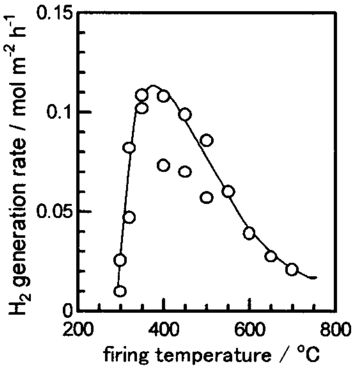

Fig. 6 Change in H_2 generation rate with firing temperature.

in H_2 generation rate up to 400 °C is considered to be due to the crystallization of amorphous TiO_2 into the photoactive anatase phase. However, it is not clear as to why the rate decreased above 450 °C considering that the crystalline phase of the thin film was not photoinactive rutile but was still anatase. Also, a sharp growth in anatase crystallite size was not observed. Changes in crystallite size affect the band gap energy and the charge potential thereby influencing the overall photocatalytic properties.

Other possible causes of the decrease of photocatalytic activity above 450 °C are the effects of the structural changes of the silica gel layer and TiO_2 layer upon polycondensation or sintering among SiO_2 or TiO_2 fine particles.

In the former case, the gel obtained from Snowtex N is known to sinter above 800 °C from its company's catalogue. Further, in our previous photocatalytic work on the silica gel containing anatase fine articles, the photocatalytic activity also decreased above 500 °C, though the crystalline phase was unchanged at this temperature and the porous structure of the material was retained up to 800 °C.[2] Considering the above information and our observations the porous structure of silica gel layer was also unchanged up to 800 °C, therefore, the silica gel layer is not responsible for the decrease of photocatalytic properties.

A structural change of the TiO_2 layer would result in grain growth and/or decrease of the concentration of surface OH groups and lattice defects such as Ti^{3+} and might affect the photocatalytic activity.[18,19] In order to investigate the change of fine structure of the thin film, precise observations of the surface and the cross-section of the thin film are required. However, at present, it is difficult to observe such precise fine structure of the film by use of our SEM system. As mentioned already, there was no evidence of grain growth from the results of XRD measurement. In order to explain the effect of firing temperature on catalytic activity, further investigations on properties of the thin films such as the number of OH groups on the TiO_2 surface and the concentration and mobility of charge carriers, are therefore necessary.

Fig. 7 shows the changes in hydrogen generation rate with film thickness for a sample heat-treated at 450 °C for 4 h. The hydrogen generation rate is presented as the rate per unit surface area as well as per unit mass of the TiO_2 sample. The sample mass was evaluated assuming the density of an anatase crystal (3.54 g cm^{-3}) based on the assumption that the film was dense. When the thickness of the film was less than *ca.* 60 nm, the rate was very low. This may be due to the formation of island textures of TiO_2 on the platinum electrode in the early stages of spin coating. It is plausible that this texture induces the reverse reaction between photogenerated active oxidant and reductant on platinum, and consequently, hampers hydrogen evolution. Further coating applications produced a uniform TiO_2 film all over the platinum surface resulting in a homogeneous spatial separation of reaction sites.

As the film thickness was increased to >60 nm, the rate increased proportionally with the film thickness, while the rate per unit mass was almost constant and was also independent of film thickness. The photogeneration rate per unit mass was about eight times that of the reference sample of platinized TiO_2 fine particles. These results strongly suggest that a similar number of photogenerated electrons per unit TiO_2 mass diffuse to the surface of the platinum electrode regardless of the depth of the film. A potential gradient at the bottom level of the

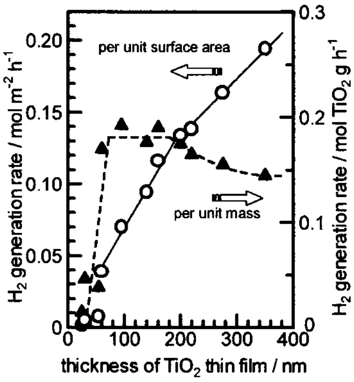

Fig. 7 Changes in H_2 generation rate with thickness of the TiO_2 thin film.

conduction band and at the top level of the valence band is probably formed across the TiO_2 layer macroscopically, because the front and reverse of the TiO_2 (n-type semiconductor) layer are in contact with the solution and platinum electrode, respectively. Therefore, photoexcited electrons diffuse to the platinum electrode and holes diffuse to the surface of TiO_2 thin film along the potential gradients. Since the film was dense and consequently had few recombination sites such as surface defects, the separation of charge carriers occurred efficiently. Furthermore, the multiple layered structure on the porous substrate prohibited the reverse reaction between photoproduced oxidant and reductant thus achieving a high photocatalytic activity as evidenced by the results obtained in this study.

Conclusions

A multilayered TiO_2 thin film photocatalyst was prepared by sol–gel and sputtering methods. Compared with the reference platinized TiO_2 powder sample, the heat-treated photocatalyst showed a high efficiency for H_2 generation from an aqueous solution of ethanol. The high catalytic activity of this thin film system was achieved by a judicious arrangement of the TiO_2 film and the platinum electrode on a porous substrate. This mesoscopic scale structure resulted in the reduction of the diffusion distances of charge carriers and the separation of redox reaction sites.

Most photocatalytic systems for environmental use will be fabricated with TiO_2 fine particles and porous support materials in commercial or industrial applications. In these systems, micropores in the system act as adsorbents of pollutants; however, poisoning or fouling easily occurs by the adsorption of not only the pollutant but also some components in the reaction system.

Because our fabricated material has a smooth surface TiO_2 layer (*i.e.* oxidation sites), the likelihood of fouling is relatively low on this side. On the other hand, the platinum surface (*i.e.* reduction site) is located on the bottom of porous substrate. However, the thickness of the substrate is only *ca.* 60 μm, therefore, the adsorbates are readily removed by washing or burning away. Further, since the redox reaction sites are spatially separated in our material, we need only to use one reaction surface of the fabricated material for an adequate reaction system and good arrangement of apparatus. Any problems on the reduction site in this material are not so important as oxidative processes, such as the removal of organic substances from polluted water and NO_x from the atmosphere by photo-oxidation, would be the main applications of this catalyst.

Although poisoning or fouling of the surface by dense pollutants is not completely avoidable in this material, our fabricated system has potential for application to the removal of pollutants from the environment in comparison to finely divided particulate photocatalysts in porous media.

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