Preparation of tabular TiO$_2$–SrTiO$_3$–$_8$ composite for photocatalytic electrode

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Received 29 August 2003; revised 17 September 2003; accepted 26 September 2003

Abstract

To improve the efficiency of photo-induced reactions, the recombination of photogenerated electrons and holes in semiconductor must be suppressed. We have proposed that the utilisation of n$^+/n$ heterogeneous junction which yields a large potential gradient in the junction region. Up to now, we have studied the superiority of such junctions in the photocatalytic reaction using composite particles consisting of TiO$_2$ and several alkaline-earth titanates. In this study, the preparation of tabular composite consisting of TiO$_2$ and SrTiO$_3$–$_8$ was examined focusing on morphologies and crystallographic features of oxides. The ideal configuration of tabular composite is the layered structure of n-type TiO$_2$/n$^+$-type semiconductor/metal or the mixed one partially containing such structure pass. The tabular composite was prepared by an oxidation of metallic Ti chips covered with SrCO$_3$ powder. By such simple preparation method, the composite with designed oxides such as TiO$_2$ and SrTiO$_3$–$_8$ was obtained on the Ti substrates. The grain size and the volume fraction of constituent oxides depend strongly on the oxidation temperature. When the composite is prepared at 1173 K, the grain size of oxides is measured to be about 0.5–1.0 $\mu$m. In contrast, a remarkable grain coarsening and an increase in the volume fraction of TiO$_2$ can be observed in the oxidation at 1273 K. Furthermore, the developed texture of composite was strongly influenced by that of the Ti substrates and the oxidation temperature. Thin TiO$_2$ layer on the surface of SrTiO$_3$–$_8$ phase was prepared by acid solution treatment, the designed configuration of composites could be obtained.

Keywords: Strontium titanate; Photocatalyst; Tabular electrode; Composite; Microstructure; Texture

1. Introduction

Since photo-assisted water splitting into hydrogen and oxygen on titanium dioxide (TiO$_2$) was demonstrated by Fujishima and Honda [1,2], the reaction has been widely investigated because it has a great potential to settle serious energy and environmental issues. Although, the photocatalytic reactions are finding wide applications today in various fields such as sterilisation and air purifying, the photo-assisted water splitting is not yet realised as a practical application because of low efficiency. For a breakthrough in this technology, we must conquer following two difficulties; a high efficient charge separation of photogenerated electrons and holes, and a photo-excitation of the charges by a visible light. Up to now, most of researchers have focused on anatase-type TiO$_2$ [3], which exerts relatively high photocatalytic activity under the light irradiation with wave length of $\lambda < 390$ nm and high chemical stability.

To improve the efficiency of photo-induced reactions, the recombination of photogenerated electrons and holes in semiconductor must be suppressed. Recently, some of researchers have realised a limitation of TiO$_2$ alone for further improvement of photocatalytic efficiency. A well-known approach for breaking the deadlocks is to load cocatalyst, e.g. NiO, Pt and RuO$_2$ on TiO$_2$, which bring to separate photogenerated electrons and holes. Similarly, it is known to use composite films and powders consisting of two semiconducting photocatalysts, e.g. TiO$_2$/GaP [4], TiO$_2$/Nb$_2$O$_5$ [5], TiO$_2$/SnO$_2$ [6], TiO$_2$/WO$_3$ [7,8]. We also reported about the superiority of composites in photocatalytic efficiency [9,10]; the photocatalytic reactions were activated by the composite particles consisting of TiO$_2$ and acceptor-doped perovskite-type oxide Sr(2Zr$_1$–$Y$)$_2$O$_3$–$_8$ even under the irradiation of visible light [10]. Thus, the composites have a great potential to overcome...
the difficulties. We have inferred that the key factor for the improvement of photocatalytic efficiency is the appropriate energy band control such as producing the large potential gradient at heterogeneous semiconductor junctions and inducing the impurity levels.

From viewpoint of the practical uses, the powder photocatalysts have a serious limitation. So, it is urgently necessary for us to prepare tabular or shaped photocatalysts. Actually, many researchers have proposed several preparation methods of the shaped photocatalysts. However, most of them were employed the application of TiO2 as thin films on the substrates [11]. We believe that the development of new preparing method makes the available materials wide.

The purpose of this work is to investigate the effect of heterogeneous semiconductor junction showing the large potential gradient on the photocatalytic activity. In addition, a preparing of tabular composite electrodes with such heterogeneous junction was also examined.

2. Theoretical consideration

In the vicinity of heterogeneous junctions of semiconductors, a diffusion potential appears depending on the electronic character of the constituents such as energy band structures and Fermi levels. As is well known, a solar cell is constructed by a p-type and an n-type silicon semiconductor. Both semiconductors show equivalent valence band maximum and conduction band minimum because of same matrix. However, they show different Fermi levels; that in the n-type is higher than that in the p-type. Electrons and holes diffuse into the p-region and the n-region from the original, respectively, so as to have equivalent Fermi level in two types of semiconductors. As a result, the diffusion potential appears in the junction region.

When n-type semiconductor electrode is immersed in an aqueous solution, an uphill diffusion potential toward the aqueous solution is known to appear in their surface region. Using the heterogeneous junction of an n-type semiconductor contacts an aqueous solution, an uphill diffusion potential toward the aqueous solution is known to appear in their surface region. Actually, many researchers have proposed several preparation methods of the shaped photocatalysts. However, most of them were employed the application of TiO2 as thin films on the substrates [11]. We believe that the development of new preparing method makes the available materials wide.

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When n-type semiconductor electrode is immersed in an aqueous solution, an uphill diffusion potential toward the aqueous solution is known to appear in their surface region. Then, we consider the construction of diffusion potential using the heterogeneous junction of an n-type semiconductor and an n-type semiconductor as shown in Fig. 1, where the n-type semiconductor contacts an aqueous solution. If the Fermi level of the n-type semiconductor is higher than that of the n-type semiconductor, a diffusion potential appears in the junction region based on the above-mentioned mechanism. As a result, a large diffusion potential with a monotonic uphill slope can be generated through the n-type semiconductor because the potential slopes in both junction regions have the same sign. The photo-induced electrons and holes are immediately separated by the large electric field.

TiO2 of the n-type semiconductor has been focused because it exerts a relatively high photocatalytic activity under the light irradiation with wave length of λ < 390 nm and a high chemical stability. Therefore, TiO2 is the most likely candidate for the n-type semiconductors of our designed composite. On the other hand, the n-type semiconductor is required to have a higher Fermi level than n-type TiO2. Moreover, the valence band maximum and the conduction band minimum in the n-type semiconductor is desirable to be equivalent to those in TiO2 in order to obtain a smooth diffusion potential gradient. Thus, an ideal junction of semiconductor with large potential gradient can be proposed. However, one may believe that it is unrealistic to find out a suitable n-type oxide, the Fermi level of which is higher than that of TiO2.

The donor-doped alkaline-earth titanates with a perovskite structure have been also investigated. According to a recent report [12], the Fermi level of La3+-doped SrTiO3 or perovskite-type titanates with oxygen deficient situates above the conduction band minimum. That is, such titanates are expected to be the n-type semiconductors. On the other hand, the conduction band minimum and the valence band maximum in the alkaline-earth titanates is nearly equal to those in TiO2. The energy band gaps for SrTiO3, BaTiO3, anatase-type TiO2 and rutile-type TiO2 are 3.2, 3.0, 3.0 and 3.2 eV, respectively. Thus, the donor-doped alkaline-earth titanates have an enough potential as the n-type semiconductor of a companion to TiO2.

When most of the dopant such as La3+ in the Sr or Ba site, Nb5++ in the Ti site, V3+ and V5+ works as a donor to yield electrons in SrTiO3 or BaTiO3, the titanates may become black and show a metal-like conductivity. The oxygen vacancies are considered to yield electrons as follows

\[ \text{O}_6^0 \rightarrow V_{O} + 2e^0 + 1/2O_2 \]  
\[ \text{O}_6^0 \rightarrow V_{O} + e^0 + 1/2O_2 \]

According to our experience, however, the dopant contributes to produce defects in the cation and anion site of the perovskite phase under appropriate preparing conditions. The titanates become colored due to electronic transitions via impurity defect levels, maintaining semiconductor properties. We infer that the Fermi level of donor doped alkaline-earth titanates depends on the preparation conditions of samples.
Thus, if we succeed in preparing the composite of semiconductors with the $n^+/n$ heterogeneous junction, the large potential gradient would appear in the junction region. It must improve the photocatalytic activity. This consideration is quite new and has a great potential for it, the detail was discussed in our previous paper [13].

3. Experimental procedure

3.1. Preparation of composite powders

As the $n^+$-type semiconducting oxide, we selected the perovskite-type SrTiO$_3\_\delta$ oxide and synthesised it by a conventional method [13] using powdered raw materials of SrCO$_3$ (4N) and TiO$_2$ (4N). To produce SrTiO$_3\_\delta$/TiO$_2$ composite from SrTiO$_3\_\delta$ alone, the obtained powder was pickled with 1 M HNO$_3$ aqueous solution for 20 min at 353–363 K. The pickled particles were successively washed with distilled water and dried at 413 K for 1 h. On the other hand, the commercial fine powder of anatase-type TiO$_2$ (Ishihara Sangyo, ST-01) was also purchased for comparison.

3.2. Preparation of tabular composite on Ti substrate

Based on the proposed consideration, the ideal configuration of tabular composite is the layered structure of $n$-type TiO$_2$/$n^+$-type semiconductor/metal. The tabular composite consisting of TiO$_2$ and SrTiO$_3\_\delta$ was prepared on Ti substrates by a simple method. The pure Ti chip (3N, 8 $\times$ 8 mm$^2$ $\times$ 2 mm) finished on #800 emery paper was covered with SrCO$_3$ powder dispersed in ethanol. After drying, the samples were annealed at 1173 or 1273 K for 3 h in air. The residual SrCO$_3$ powder or its oxides were swept from the surface with cotton. Some composite plates were pickled with 5 M HNO$_3$ aqueous solution for 2 h to construct the TiO$_2$ layer on the surface of SrTiO$_3\_\delta$.

3.3. Characterisation of samples and evaluation of photocatalytic activity

The X-ray diffraction (XRD, employing Cu K$_\alpha$ radiation) analysis was carried out in order to determine the constituents, the volume fraction and texture of them. The optical absorption properties of the sample powder were evaluated from their diffuse reflectivity recorded by a double-beam spectrophotometer equipped with a white-coated (MgO) integrated sphere. MgO powder was used as a reference material.

The photocatalytic activity of the sample powder was evaluated by a photodegradation of methylene blue aqueous solutions [9,10,14]. The $2 \times 10^{-5}$ M methylene blue aqueous solution (100 ml) was prepared, whose maximum absorbance at approximately 664 nm situates between 1.50 and 1.55 cm$^{-1}$. The aqueous solution (100 ml) containing the sample powder (0.20 g) was loaded in a glass container and then set in a water-cooling bath. The sample powder was dispersed in the solution using magnetic stirrer. After dispersing for 1 min in a dark enclosure, an irradiation of 500 W Xe discharge light through a slit of 28 cm$^2$ was introduced. To examine the effect of the irradiation of light and the visible light ($\lambda > 420$ nm) on the photobleaching of methylene blue solution, the period without the discharge light and with a UV-cut filter was suitably inserted. At predetermined time, the optical absorption spectrum for the supernatant solution was recorded using a double-beam spectrophotometer.

4. Result and discussion

4.1. Photocatalytic activity of composite particles

The perovskite oxide, SrTiO$_3\_\delta$ powder was prepared by the conventional ceramic method. The optical absorption of the powder was evaluated from the diffuse reflectivity. The absorption in the range of 400–600 nm was confirmed and it may be attributed to the colorations induced by the oxygen defects [13]. This implied that the powder is the $n^+$-type semiconductor. When the powder was pickled with 1 M HNO$_3$ aqueous solution for 20 min, remarkable changes in the XRD profiles could not be confirmed. As reported before [13], however, the XRD diffraction peaks of TiO$_2$ in commercial SrTiO$_3$ powders (TPL Inc.) slightly but clearly increased by the pickling with nitric acid or hydrochloric acid aqueous solution. On the other hand, the formation of thin TiO$_2$ on the surface of BaTiO$_3$ by the treatment with acid solution was reported [15]. So, the present particles must be fully or partially coated by thin TiO$_2$. We inferred that the formed TiO$_2$ phase on the surface may be too thin to be detected by XRD analysis because the treatment time of the pickling is short. The photobleaching of methylene blue aqueous solution was carried out to estimate the photocatalytic efficiency of the composite particles. As is well known, the aqueous solution sustains the photocatalytic redox reactions sensitised by anatase-type TiO$_2$, the characteristic absorption peak of methylene blue at approximately 664 nm decreases smoothly with a slight shift toward a shorter wave length, and the solution eventually becomes colorless. Fig. 2 shows the variations in maximum absorbance between 600 and 664 nm by the light irradiation are plotted against time for anatase-type TiO$_2$ (ST-01) powder, SrTiO$_3\_\delta$ powders with and without pickling treatment. In this figure, the solid and the dashed-and-dotted lines are corresponding to the irradiation of Xe discharge light and visible light with $\lambda > 420$ nm using L42 sharp-cut filter, respectively. On the other hand, the broken line indicates interruption of the irradiation. The degradation of methylene blue solution is caused by the photocatalytic reactions since the decrease in absorbance clearly reacts to the irradiation light in all
employed powders. The photocatalytic activity of the alkaline-earth titanate powders is fairly weak compared with that of the TiO₂ (ST-01). In contrast, the photobleaching under the irradiation of Xe light is actually accelerated by the SrTiO₃ with the acid solution treatment. These results imply the appearance of the large potential gradient caused by the n⁺/n junction; we could show the validity of our proposed principle about the improvement of photocatalytic efficiency using the heterogeneous semiconductor junction.

On the other hand, the photobleaching of methylene blue aqueous solution sensitised by the donor-doped alkaline-earth titanates, Sr(Ti₀.₉₅Nb₀.₀₅)O₃₊δ, was examined in the previous paper [13]; the degradation rate is effectively sensitised by it even under the irradiation of visible light. A doping impurity in semiconductors is known to bring not only an increasing in the electrical conductivity but also the absorption of visible light due to electron transition via impurity levels. We have supposed that the holes photoexited by visible light in Sr(Ti₀.₉₅Nb₀.₀₅)O₃₊δ move to the surface through n-type TiO₂ layer.

Thus, the composites have a great potential for the improvement of photocatalytic efficiency because they show good photobleaching property of methylene blue aqueous solution due to the large potential gradient and have a possibility to give a special property for each constituent.

4.2. Preparation of tabular composite electrodes

We could confirm the priority of the n⁺/n junction on the photocatalytic reaction in the composite particles of semiconductors. Then, the photocatalytic electrode consisting of the same constituents such as TiO₂ and SrTiO₃ was prepared by simple method; the Ti chips coated with SrCO₃ powder were annealed in air. Then, the residual SrCO₃ powder and its oxides were removed from the surface with cottons. Fig. 3 shows the XRD patterns for the tabular composite prepared on Ti substrate at (a) 1173 K and (b) 1273 K for 3 h. All diffraction peaks can be identified as those for rutile-type TiO₂ or perovskite-type SrTiO₃ in spite of the oxidation temperature, though small peaks of the residual SrCO₃ can be confirmed. We could obtain SrTiO₃ phase on the Ti substrates by such simple method. However, the volume fraction of both titanates seems to depend on the temperature. Then, in order to estimate the change in the volume fraction of both titanates depending on the oxidation temperature, the following intensity ratio of XRD peaks for SrTiO₃ (STO) to that for all titanates, \( f_{STO} \), was calculated at each temperature

\[
f_{STO} = \frac{\sum I_{STO}}{\sum I_{titanates}}
\]

From the XRD profiles in Fig. 3, the intensity ratios at 1173 K and at 1273 K were obtained to be \( f_{STO}^{1173} = 0.071 \) and \( f_{STO}^{1273} = 0.032 \), respectively. The \( f_{STO}^{1173} \) was 2.2 times larger than that at 1273 K. It is conjectured that the formation rate of TiO₂ is drastically increased with rise in temperature compared with that of SrTiO₃. This result suggests that the oxidation at too high temperature is less favourable for preparation of composite containing a large amount of SrTiO₃. Fig. 4 shows the SEM images of titanates prepared by oxidation of metallic Ti chips covered with SrCO₃ powder at 1173 K (a), (b) and 1273 K (c) for 3 h in air. Image of (d) is for the oxidation of Ti alone at 1273 K. Their morphologies of titanates are strongly influenced by the oxidation temperature. When the composite is prepared at 1173 K, the grain size is measured...
to be about 0.5 μm as shown in Fig. 4(a) and (b). In contrast, a remarkable grain coarsening can be confirmed in the oxidation at 1273 K (Fig. 4(c)). On the other hand, such morphologies of composites are quite different from that of TiO₂ formed by the oxidation of Ti alone as shown in Fig. 4(d). Thus, the volume fraction and morphology of oxide composites are found to change clearly depending on the oxidation temperature.

In general, several properties of materials are strongly influenced by the crystalllographic features such as crystal orientation, grain boundary character and texture [16,17]. The photocatalytic activity of TiO₂ is also known to be very sensitive not only the photoexcited carrier behaviours but also the crystal orientation of surface [18]. So, the suitable microstructure controls should be done for increasing the photocatalytic efficiency of the materials. In multi-phase materials, on the other hand, the second phases often maintain the crystalllographic orientation relationship with the matrices. The tendency has also been confirmed in several oxides; the rutile TiO₂ (200) films are highly oriented on the (0001) plane of α-Al₂O₃ [19], as an example. Such results indicate that the crystal orientation controls of second phases can be performed by controlling the orientation of substrates. In the present study, button ingots of pure Ti (about 10 g) were prepared by arc-melting under high purity Ar gas in order to obtain textured substrates. Since, the employed metal mold was cooled with water flow, the directional solidification must occur from the bottom toward the upper surface. From the ingot, two types of plates, which are parallel or perpendicular to the direction of solidification (DS), were prepared by spark machining. Fig. 5 shows the XRD patterns of α-Ti with random orientation (a), the arc-melted sample taken parallel (b) or perpendicular (c) to the DS. The textures can be clearly confirmed to develop in the samples; the reflection of (1120) in the Ti plate parallel to the DS is significantly larger than that in the plate perpendicular to the DS, as an example. We are not concerned here with the development mechanism of texture in arc-melted Ti, but the textured samples could be easily obtained by the arc-melting. Then, such Ti plates were oxidised with SrCO₃ powders at 1273 K for 3 h in air. The XRD patterns of the obtained composites are shown in Fig. 6. In this figure, (a) and (b) are corresponding to these of perovskite SrTiO₃ and rutile TiO₂ powders as references, respectively. Although, we could not detect a remarkable change in the XRD profiles of perovskite SrTiO₃ due to the small volume fraction of it, the obtained composites surely show the different textures, particularly in TiO₂, depending on the substrates as shown in Fig. 6(c) and (d). The development of textures in the composites must be strongly influenced by the crystalllographic orientation relationships with the substrate of Ti. As shown in Fig. 3, on the other hand, the texture development of composites seems to be changed depending on the annealing temperature; several reflection intensity of rutile TiO₂ changes with rise in temperature in spite of using equivalent textured Ti substrates. These results imply that the controls of substrate texture and oxidation temperature are so effective to control the crystalllographic features of composites. Using this method, we can prepare an appropriate crystal orientation of surface plane which is the most important parts for the photocatalytic electrodes.

Furthermore, the smooth flow of the photoexcited charges through the heterogeneous junction must require a coherent boundary between the two different semiconductors,
because the lattice defects may become the favourable trap or recombination site of electrons and holes. According to recent reports, the surface structure of SrTiO3 shows the similar arrangement of TiO2 [20,21]. This means that the coherent interface can be existed between TiO2 and SrTiO3, and the formed interfaces seem to be limited by the orientation relationship between them. So, to construct the ideal configuration of composites, the crystallographic orientation relationships among TiO2, SrTiO3 and Ti must be discussed. Now, we continue to analyse the details in crystallographic futures.

To obtain the designed configuration of composite, thin TiO2 layer should be form on the surface of SrTiO3 phase.

5. Summary and conclusions

Effect of the heterogeneous junction on the photocatalytic reaction was examined using the acid-treated SrTiO3−δ powder with oxygen deficient. The preparation of tabular titanate composite was also examined. The following conclusions were reached.

(1) The Fermi level of the SrTiO3−δ may be higher than that of TiO2. Their conduction band minimum and valence band maximum are nearly equivalent. The mutual solubility supports the formation of a coherent heterogeneous junction.

(2) The composite powder of SrTiO3−δ powder with acid solution treatment effectively sensitises...
the photobleaching of methylene blue aqueous solution compared with the SrTiO$_3 - \delta$ single phase powder. This implies the appearance of the large potential gradient caused by the $n^+/n$ semiconductor junction.

(3) The tabular composite consisting of TiO$_2$ and SrTiO$_3$ could be obtained by the oxidation of Ti chip coated with SrCO$_3$ powder in air. The morphology and volume fraction of constituents were strongly influenced by the oxidation temperature. The control of substrate texture is a useful method of preparing photocatalytic electrode with an appropriate surface orientation. In addition, the acid solution treatment contributes to expanding surface area of tabular composite and constructing thin TiO$_2$ layer on SrTiO$_3$ which leads to obtain the desired configuration of composite for photocatalytic electrode with the large potential gradient.

Acknowledgements

This work was supported by ‘Priority Assistance of the Formation of Worldwide Renowned Centers of Research—The 21st Century COE Program (Project: Center of Excellence for Advanced Structural and Functional Materials Design)’ from the Ministry of Education, Sports, Culture, Science and Technology of Japan. This work was also supported by a Research Grant from the Iron and Steel Institute of Japan.

The authors would like to express thanks to Mr Uchibayashi, Mr Okamoto and Mr Tanaka for their experimental assistance.

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