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Visible light-induced photobleaching of methylene blue aqueous solution using $(Sr_{1-x}La_x)TiO_{3+\delta}$–$TiO_2$ composite powder

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Abstract

We have investigated the charge flow through heterojunction, which consists of two semiconductors possessing the equivalent energies of the conduction band edges as well as the valence band edges. The composite powders possessing heterogeneous microjunctions prepared by precipitating anatase-type TiO_2 layers on perovskite-type $(Sr_{0.95}La_{0.05})TiO_{3+\delta}$ particles from $TiOSO_4$ aqueous solution; the $(Sr_{0.95}La_{0.05})TiO_{3+\delta}$ powder absorbed light with $\lambda < 550$ nm. Under visible light irradiation with $\lambda > 420$ nm of Xe discharge, the photobleaching of methylene blue aqueous solution sensitized using the composite proceeded several times faster than that using TiO_2 alone. The change in the absorption spectrum shape of methylene blue aqueous solution with irradiation time differed significantly from that obtained using TiO_2 alone. The results have revealed that the uphill energy band bending in the composite was steeper than that in TiO_2 alone, and the photogenerated hole was predominantly supplied to methylene blue ions.

Keywords: Heterojunction; Strontium titanate; Photocatalyst; Composite particle; Photobleaching; Methylene blue

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1. Introduction

Since the discovery of the photoelectrochemical water splitting on n-type TiO_2 [1], i.e. photoelectrode, solar energy conversion to hydrogen and electricity using the photogenerated charges has received much attention [2–7]. The applications of the photogenerated charges include the photodegradation of organic molecules present in polluted water and air [8,9] and wet solar cells sensitized by organic dyes [10]. To attain efficient reactions, the photogenerated electron and hole in the semiconductors must be spatially separated as fast as possible and then transferred into the reactants; otherwise the charges may be recombined. Well-known approaches for the spatial charge separation are to load cocatalysts, e.g. NiO, Pt, and RuO_2 on TiO_2 and also to use composite films and powders consisting of two semiconducting photocatalysts, e.g. TiO_2/GaP [11], TiO_2/Nb_2O_5 [12], TiO_2/SnO_2 [13–15], TiO_2/WO_3 [16–18], and TiO_2/CdS [19,20]. When considering the application to the photoelectrochemical water splitting and wet solar cell, the charge separation must proceed in one-dimensional. We may refer to solar cells using p- and n-type silicones, i.e. p–n homojuctions [21], which have achieved a great success in solar energy conversion to electricity. The difference between the Fermi levels of two semiconductors yields energy band bending in the junction region, which results in one-dimensional separation of the photogenerated electron and hole. The energy step and spike at the junction interface, leading to the charges' recombination, do not appear in the case of the homojunction.

We have investigated a heterogeneous microjunction consisting of perovskite-type $(Sr_{1-x}La_x)TiO_{3+\delta}$ ($E_g = 3.2$ eV) and anatase-type TiO_2 (E_g=3.2 eV); that is an n^+/n junction. Because they possess the equivalent energies of the conduction band edges as well as the valence band edges, the situation becomes similar to that for homojunction. In the present study, the composite powders, i.e. $(Sr_{0.95}La_{0.05})TiO_{3+\delta}$ particles covered by anatase-type TiO_2 layers, were prepared, together with TiO_2 powder alone. It is well-known for TiO_2 plate dipped in aqueous solution that an uphill energy band bending occurs in the surface region [1]. We carried out the photobleaching of methylene blue sensitized using the composite powder and TiO_2 powder alone, and discussed the effect of the heterojunction on the uphill band bending and charge separation.

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2. Experimental procedure

2.1. Materials

The $(Sr_{0.95}La_{0.05})TiO_{3+\delta}$ used in this study was synthesized by the conventional solid-state reaction method. The powdered raw materials used were $SrCO_3$ (4N) and TiO_2 (4N) purchased from Rare Metallic Co. Ltd., and reagent-grade $LaCl_3{\cdot}7H_2O$ purchased from Kanto Kagaku Co. Ltd. The raw materials were weighed considering ignition losses, and mixed using a planetary ball mill with 80 cm^3 pots made of partially stabilized zirconia. In order to ensure thorough mixing of the powders, ethanol was added during the mixing operation. After the dried mixtures were calcined at 1073 K for 10 h, the calcined powders were mixed again using the planetary ball mill and pressed into 17.2-mm diameter disks under 265 MPa. The disks were subsequently loaded in a Pt crucible and sintered at 1573 K for 10 h. The disks were then crushed and pulverized using the planetary ball mill. To attain an n^+/n junction, the obtained powder (1 g) was first dispersed in 1 mol/dm^3 HNO_3 acid solution (50 cm^3) maintained at 353–363 K. After 20 min, $TiOSO_4$ powder (0.2 g) dissolved in 1 mol/dm^3 HNO_3 acid solution (10 cm^3) was added, and 1 mol/dm^3 ammonia aqueous solution (70 cm^3) successively added in the solution with stirring; pH 0.75–0.85 was attained. In this manner, the $(Sr_{0.95}La_{0.05})TiO_{3+\delta}$ particles were coated by TiO_2 sol, the amount of which was 10 mass% for the largest of the core particles. Sulfur was removed totally before drying by washing with purified water. The composite powder was then annealed at 873 K for 1 h, so that the sol could become TiO_2 particles. For comparison, the $SrTiO_3$ powder and anatase-type TiO_2 fine powder were prepared by a similar solid-state reaction method and precipitating from $TiOSO_4$ solution, respectively. The anatase-type TiO_2 powder (ST-01), supplied from Ishihara Sangyo Co. Ltd. was also used for comparison. Because the results using the TiO_2 prepared by the precipitation were completely consistent with those using ST-01, only the latter ones are presented in this paper.

The samples were subjected to powder X-ray diffraction (XRD) analysis (Cu Kα radiation using a curved graphite Kβ filter, 40 kV and 200 mA) (MXP18, MAC Science, Yokohama, Japan). The optical absorption properties of the powdered samples were evaluated from their diffuse reflectivity recorded by a double-beam spectrophotometer (Hitachi U-4000) equipped with a white-coated (MgO) integrated sphere. MgO powder was used as a reference material.

2.2. Evaluation of photocatalytic activity

The photocatalytic behavior of the sample powders was evaluated by the photobleaching of methylene blue aqueous solution containing the sample powders [22,23]. A 2×10^{-5} mol/dm^3 methylene blue aqueous solution was prepared; its maximum absorbance at approximately 664 nm lay between 1.50 and 1.55. The sample powder (0.20 g) was dispersed in the aqueous solution (100 ml) by stirring with a magnetic stirrer. After 1 min, irradiation with a 500 W Xe discharge light above the aqueous solution was initiated. After a predetermined time, 12 ml of the solution was aspirated and centrifuged. The optical absorption spectrum for the supernatant solution was recorded using a double-beam spectrophotometer (Hitachi U4000). At an appropriate interval of time, a UV-cut filter (Suruga Seiki L42) was inserted, and the photobleaching of methylene blue under visible light ($\lambda > 420$ nm) was examined.

3. Experimental results

Fig. 1 shows the powder XRD pattern of the $(Sr_{0.95}La_{0.05})TiO_{3+\delta}$–$TiO_2$ composite compared with that of $(Sr_{0.95}La_{0.05})TiO_{3+\delta}$ alone. La-doped strontium titanate was a single phase of the perovskite type. For the composite, small but clear diffraction peaks due to anatase-type TiO_2 could be observed. Fig. 2 shows the diffuse reflectance spectra of $(Sr_{0.95}La_{0.05})TiO_{3+\delta}$ powders as sintered and after surface treatment with 1 mol/dm^3 HNO_3 aqueous solution for 20 min, compared with those of the $(Sr_{0.95}La_{0.05})TiO_{3+\delta}$–$TiO_2$ composite, anatase-type TiO_2 and sintered $SrTiO_3$ and $(Sr_{0.90}La_{0.10})TiO_{3+\delta}$ at 1573 K. For the 5 mol% La-doped strontium titanate, optical absorption due to electron

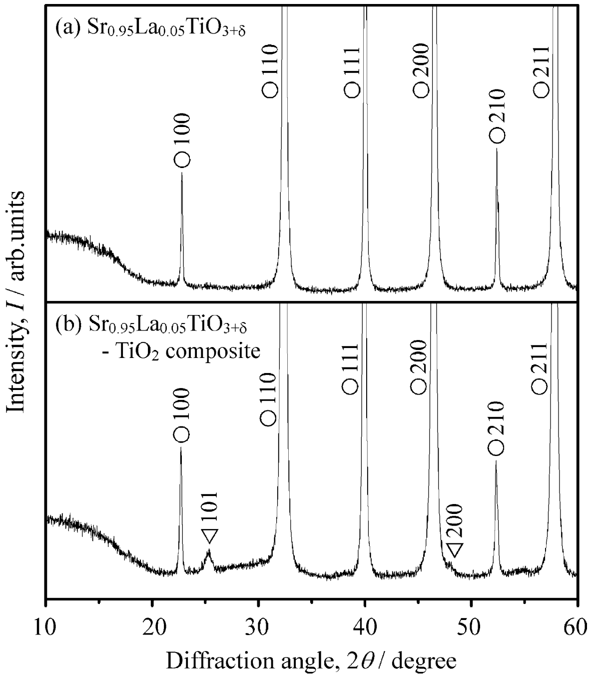

Fig. 1. Powder X-ray diffraction patterns of the $Sr_{0.95}La_{0.05}TiO_{3+\delta}$ and $Sr_{0.95}La_{0.05}TiO_{3+\delta}$–$TiO_2$ composite prepared in this study. (a) $Sr_{0.95}La_{0.05}TiO_{3+\delta}$ sintered at 1573 K (b) $Sr_{0.95}La_{0.05}TiO_{3+\delta}$–$TiO_2$ composite powder annealed at 873 K. (○) Perovskite-type $Sr_{0.95}La_{0.05}TiO_{3+\delta}$ (▽) anatase-type TiO_2.

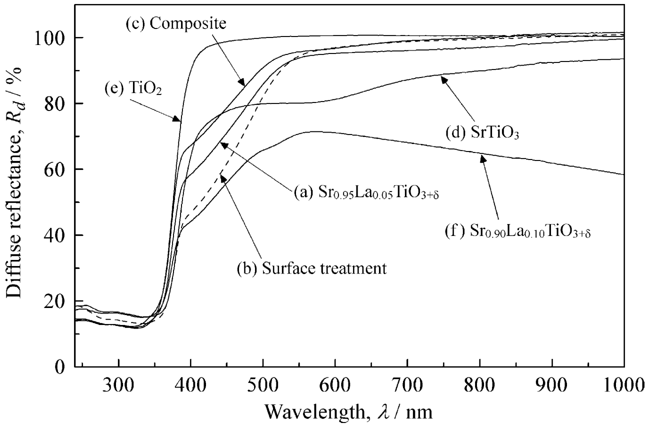

Fig. 2. Diffuse reflectance spectra of $Sr_{0.95}La_{0.05}TiO_{3+\delta}$ powder compared with those of TiO_2, $SrTiO_3$ and $Sr_{0.95}La_{0.05}TiO_{3+\delta}$–$TiO_2$ composite powders. (a) $Sr_{0.95}La_{0.05}TiO_{3+\delta}$ sintered at 1573 K (b) $Sr_{0.95}La_{0.05}TiO_{3+\delta}$ with surface treatment (1 mol/dm^3 HNO_3 aqueous solution) (c) $Sr_{0.95}La_{0.05}TiO_{3+\delta}$–$TiO_2$ composite powder (d) $SrTiO_3$ sintered at 1573 K (e) TiO_2 (anatase-type ST-01, Ishihara Sangyo Co. Ltd.) (f) $Sr_{0.90}La_{0.10}TiO_{3+\delta}$ sintered at 1573 K.

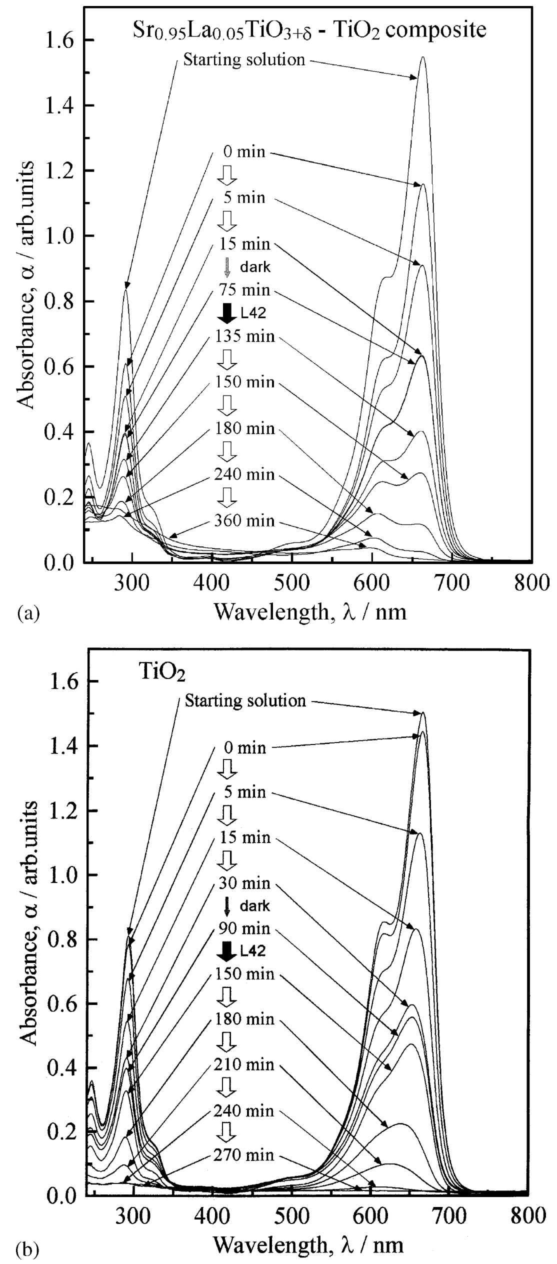

Fig. 3. Variation in the absorption spectra of methylene blue aqueous solution sensitized using $Sr_{0.95}La_{0.05}TiO_{3+\delta}$–$TiO_2$ composite powder, compared with those using TiO_2 powder alone under irradiation with 500 W Xe discharge light. The concentration of methylene blue in the starting solution was 2.0×10^{-5} mol/dm^3. (⬇) irradiation with visible light of $\lambda > 420$ nm using a UV-cut filter (L42, Suruga Seiki Co. Ltd.). (⇩) unfiltered irradiation. (a) $Sr_{0.95}La_{0.05}TiO_{3+\delta}$–$TiO_2$ composite powder (b) TiO_2 powder alone.

transition via impurity level (approximately 2.9 eV, 430 nm) was observed together with fundamental absorption. As a result, the $(Sr_{0.95}La_{0.05})TiO_{3+\delta}$ absorbed light with a long wavelength of 550 nm. When it was subjected to HNO_3 or HCl surface treatment, the optical absorption rate was slightly increased; this was attributable to an increase in its surface roughness [24]. When most of the doped La^{3+} in the Sr site works as a donor to yield excess electrons, the titanate becomes a black metal-like conductor. However, the $(Sr_{0.95}La_{0.05})TiO_{3+\delta}$ prepared in the present study was colored due to electronic transitions via impurity defect levels, maintaining a semiconductive property. Thus, we inferred that most of the doped La was used in producing defects in the cation site of the perovskite phase. When the amount of the doped La was as large as 10 mol%, optical absorption due to electron in the conduction band was observed, and the sample became pale gray.

Fig. 3 shows variation in the absorption spectra of methylene blue aqueous solution sensitized using the $(Sr_{0.95}La_{0.05})TiO_{3+\delta}$–$TiO_2$ composite powder, compared with that using TiO_2 alone, under irradiation with Xe discharge light. It is well-known that, as shown in Fig. 3(b), when the aqueous solution sustains the photocatalytic redox reactions sensitized by anatase-type TiO_2, the characteristic absorption peak of methylene blue at approximately 664 nm decreases with a shift toward a shorter wavelength [22,23,25,26]. As the irradiation proceeded, the absorption spectrum exhibited finally a single small peak at approximately 600 nm. In the case of the $(Sr_{0.95}La_{0.05})TiO_{3+\delta}$–$TiO_2$ composite powder, the absorption peak of methylene blue at approximately 664 nm hardly shifted with time. Two peaks appeared on the absorption spectrum at approximately 600 and 664 nm, where the former peak was larger than the latter one. These two absorption peaks were observed until the aqueous solution became eventually colorless. In Fig. 4, variations in maximum absorbance between 600 and 664 nm of methylene blue aqueous solution sensitized using various sample powders are plotted against time. The photocatalytic activities of the $SrTiO_3$ and $(Sr_{0.95}La_{0.05})TiO_{3+\delta}$ as sintered were found to be fairly weak. When the $(Sr_{0.95}La_{0.05})TiO_{3+\delta}$–$TiO_2$ composite

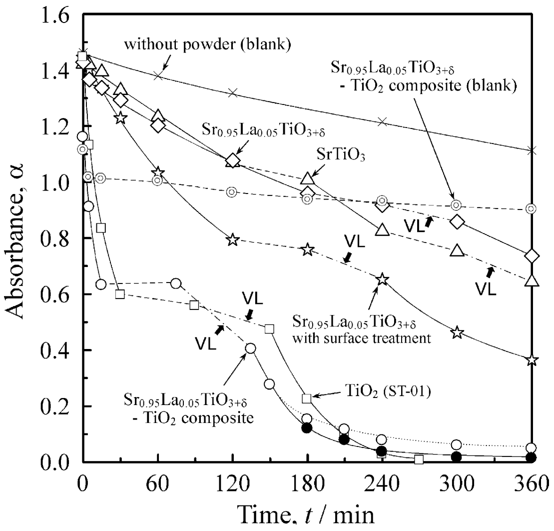

Fig. 4. Change in maximum absorbance in the wavelength range of 600–664 nm sensitized using various sample powders under irradiation with 500 W Xe discharge light. Chain line (↓ **VL**) indicate irradiation with visible light of λ > 420 nm using a UV-cut filter (L42, Suruga Seiki Co. Ltd.). Solid line indicates unfiltered irradiation. Dotted line indicates interruption of irradiation. (△) $SrTiO_3$ powder prepared at 1573 K (◇) $Sr_{0.95}La_{0.05}TiO_{3+\delta}$ prepared at 1573 K (☆) $Sr_{0.95}La_{0.05}TiO_{3+\delta}$ with surface treatment (1 mol/dm^3 HNO_3 aqueous solution) (○, ●) $Sr_{0.95}La_{0.05}TiO_{3+\delta}$–$TiO_2$ composite (maximum values in the range of 600–664 nm and at approximately 664 nm, respectively) (□) TiO_2(ST-01) powder dried at 413 K (×) without sample powders (blank test with unfiltered irradiation) (◎) $Sr_{0.95}La_{0.05}TiO_{3+\delta}$–$TiO_2$ composite (blank test without irradiation).

powder was used as a sample, the absorbance of methylene blue smoothly decreased similarly to that of methylene blue sensitized using TiO_2 alone. When the irradiation was interrupted, the decrease in absorbance became negligibly small. Immediately before the interruption, the rate of decrease in absorbance under unfiltered irradiation, i.e. $\Delta_{abs} = 0.028\,min^{-1}$ was twice as large as that using TiO_2 alone, i.e. $\Delta_{abs} = 0.015\,min^{-1}$. When the visible light of λ > 420 nm was successively irradiated, the photobleaching proceeded smoothly again. The rate of decrease in absorbance, i.e. $\Delta_{abs} = 0.0039\,min^{-1}$ was several times larger than that using TiO_2 alone, i.e. $\Delta_{abs} = 0.00075\,min^{-1}$. The rate of decrease with TiO_2 was evaluated based on the difference in slopes between the irradiation and its interruption because a slight decrease in the maximum absorbance was observed without irradiation. Another important feature for the $(Sr_{0.95}La_{0.05})TiO_{3+\delta}$–$TiO_2$ composite powder is that, the absorbance of the methylene blue aqueous solution at 0 min; that is, 1 min after dispersal of the powder, is significantly lower than that of the as-prepared solution, i.e. between 1.50 and 1.55. This may come from the adsorption of methylene blue ions on the sample surface; the adsorption appeared to be almost terminated before the irradiation with Xe discharge. The result implies that the composite powder was charged up due to spatial charge separation in it.

4. Discussion

As shown in Fig. 4, the $(Sr_{0.95}La_{0.05})TiO_{3+\delta}$–$TiO_2$ composite powder, i.e. $(Sr_{0.95}La_{0.05})TiO_{3+\delta}$ particles covered by a thin TiO_2 layer exerted a high photocatalytic activity under visible light of λ > 420 nm. Anatase-type TiO_2 hardly absorbs visible light of λ > 410 nm. Under irradiation of λ < 410 nm, the photocatalytic activity of TiO_2 is much higher than that of $(Sr_{0.95}La_{0.05})TiO_{3+\delta}$ alone. These results imply that the photogenerated charge, i.e. electron or hole, in the $(Sr_{0.95}La_{0.05})TiO_{3+\delta}$ moved in the TiO_2. As shown in Fig. 3, the variation in the absorbance spectra of methylene blue aqueous solution obtained using $(Sr_{0.95}La_{0.05})TiO_{3+\delta}$–$TiO_2$ composite was significantly different from that obtained using TiO_2 alone. Fig. 5 shows a plausible degradation scheme of methylene blue [26,27]. When the photogenerated electrons are predominantly supplied to methylene blue, colorless leuco-MB is formed, and therefore the absorption peaks in the range of 600–664 nm must decrease with time keeping the original shape of methylene blue. If the successive degradation reactions via *N*-demethylation induced by holes are relatively slow, the MB aqueous solution must become colorless once [26]. Thereafter, the absorption peak at approximately 600 nm must appear and increase gradually; this may be the case for κ-$CeZrO_4$ [28]. For instance, thionine being one of the materials formed by *N*-demethylation absorbs light with 596 nm [27,29]. As these successive degradation reactions via *N*-demethylation accelerate, that is, they occur spontaneously with the formation of leuco-MB, the absorption peak at 664 nm of methylene blue decreases with a shift toward 600 nm and disappears eventually; this is the well-known case for TiO_2 alone. If the photogenerated holes could be predominantly supplied to methylene blue, the degradation reactions via *N*-demethylation would proceed without the formation of leuco-MB. On the way of the reactions, molecules formed by *N*-demethylation such as thionine coexist with methylene blue in the solution. Thus, two absorption peaks at approximately 600 and 664 nm must be observed until the methylene blue is completely decomposed. This expected spectrum variation appears to agree with the experimental result obtained using $(Sr_{0.95}La_{0.05})TiO_{3+\delta}$–$TiO_2$ composite. One may wonder if the photogenerated electron in the methylene blue ion moved into the TiO_2 layer. However, in view the fact that the rate of decrease in absorbance using TiO_2 alone was fairly small under visible light of λ > 420 nm, this effect could be neglected.

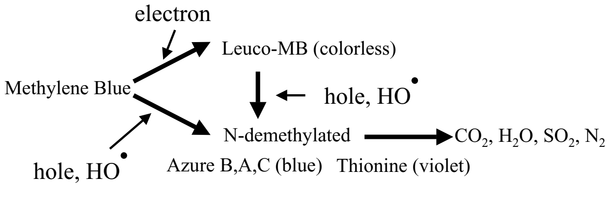

Fig. 5. Plausible photodegradation scheme of methylene blue.

For clarifying the fundamental properties of superconducting oxides, the donor-doped alkaline-earth titanates with perovskite-type structure have been extensively investigated [30–33]. According to a recent report [33], the Fermi level of $(Sr_{1-x}La_x)TiO_{3+\delta}$ becomes higher than the conduction band minimum, with increasing La content; that is, the Fermi level is located in the conduction band. In view of the fact that the $(Sr_{0.95}La_{0.05})TiO_{3+\delta}$ prepared in the present study was a semiconductor, its Fermi level might exist in the energy band gap; however, it is plausibly close to the conduction band edge. Thus, optical absorption due to electron in the conduction band was observed for $(Sr_{0.90}La_{0.10})TiO_{3+\delta}$. Because an impurity-free TiO_2 behaves as intrinsic semiconductor, the Fermi level of anatase-type TiO_2 is located in the middle of the energy band gap [34], unless it is annealed in a reducing atmosphere. Furthermore, for perovskite-type $SrTiO_3$ and anatase-type TiO_2, their conduction band minimum and valence band maximum are nearly equivalent. It is natural that their energy band gaps are equivalent; i.e. 3.2 eV for $SrTiO_3$ and 3.2 eV for anatase-type TiO_2 [9]. Thus, the energy level diagram for $(Sr_{0.95}La_{0.05})TiO_{3+\delta}$–$TiO_2$ heterojunction resembles that for homojunction where the energy step and spike at the junction interface do not appear. As shown in Fig. 6, an uphill energy band bending toward TiO_2 must be yielded in the junction region, the slope sign of which is the same as that of the energy band bending in the surface region of n-type TiO_2 dipped in the aqueous solution [35]. One may try to use a donor-doped TiO_2 plate alone with visible light response as a photochemical electrode; however, the band bending in TiO_2 becomes much smaller than that in impurity-free TiO_2 with increasing doping content [21]. In the case of the $(Sr_{0.95}La_{0.05})TiO_{3+\delta}$–$TiO_2$ composite, the diffusion potential due to the band bending in the junction region of the $(Sr_{0.95}La_{0.05})TiO_{3+\delta}$ and TiO_2 equals the difference in their Fermi levels; furthermore, the band bending in the surface region of TiO_2 contacting with the aqueous solution remains still large because of impurity-free TiO_2. Thus, a monotonic and large energy band bending, as shown in Fig. 6, may appear in a part of $(Sr_{0.95}La_{0.05})TiO_{3+\delta}$ and throughout the TiO_2 layer.

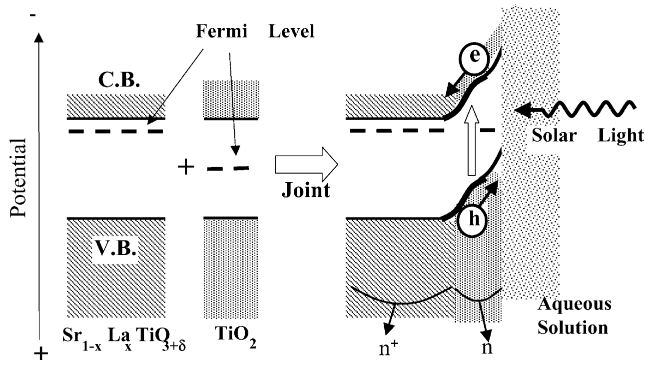

Fig. 6. Schematic drawing of idealized energy level diagram for $Sr_{0.95}La_{0.05}TiO_{3+\delta}$–$TiO_2$ heterojunction. Bold line indicates the energy band bending.

As shown in Fig. 2, the $(Sr_{0.95}La_{0.05})TiO_{3+\delta}$ prepared in the present study absorbed the light of $\lambda < 550$ nm (2.2 eV) due to its fundamental absorption and colorations induced by electronic defects. Its spectrum in the range of 500–700 nm significantly differed from that of $SrTiO_3$ sintered at 1573 K. The colorations in $SrTiO_3$ may be induced by electronic defects related to oxygen, e.g. $V_O^{\bullet\bullet}$, $V_O^{\bullet}$, $V_O^{\times}$, O_i', O_i'', $O_i^{\times}$, and $O_i^{\bullet}$. Thus, we have inferred that the colorations in $(Sr_{0.95}La_{0.05})TiO_{3+\delta}$ were induced by electronic defects related to cations, e.g. $La_{Sr}^{\bullet}$, $La_{Sr}^{\times}$, V_{Sr}'', V_{Sr}', and $V_{Sr}^{\times}$. Referring to the result shown in Fig. 2, the energy level of $La_{Sr}^{\bullet}$ and $La_{Sr}^{\times}$ may be lower by approximately 0.3 eV than the conduction band minimum. Thus, visible light of $\lambda > 410$ nm can penetrate the TiO_2 layer and induce the photoexcitation of electrons in $(Sr_{0.95}La_{0.05})TiO_{3+\delta}$ particles. The photogenerated holes move toward the surface of the TiO_2 layer along the energy band bending shown in Fig. 6. The present experimental results on photobleaching can be clearly explained by this speculation. The photogenerated electron in TiO_2 moves in the $(Sr_{0.95}La_{0.05})TiO_{3+\delta}$ particle; however, it may eventually move toward the three phase interfaces: $(Sr_{0.95}La_{0.05})TiO_{3+\delta}/TiO_2$/aqueous solution, existing in a micro-crack in the TiO_2 layer, and may then contribute slowly to catalytic reactions.

Up to date, many researchers have reported that visible-light-induced photocatalytic reactions are enhanced using composite powders and films consisting of photoactive semiconductors. However, the difference between the Fermi levels of the semiconductors that yields band bendings has hardly been considered. The smooth flow of the photogenerated charges through the heterojunction must require a coherent joint between the two semiconductors. According to a recent report, the surface top layer of $SrTiO_3$ has a TiO_2 stoichiometry with half of the TiO_5 units [36]. Furthermore, the alkaline earth titanates; e.g. $SrTiO_3$ and $BaTiO_3$ phases can dissolve trace TiO_2. These should be important factors for attaining a coherent junction. TiO_2 and alkaline earth titanates are chemically stable and abundant in resources. Their composites can be prepared by low-cost processes such as hydrothermal processes [37,38]. Because $SrTiO_3$ and $SrZrO_3$, are mutually soluble [39] and the latter energy band gap is larger than the former one, the energy band gap of $SrTiO_3$ can be increased by substituting the Ti site with Zr ions. Thus, the combination of titanium oxides with donor-doped alkaline earth titanates such as $(Sr_{1-x}La_x)TiO_{3+\delta}$ has many advantages. The principle and experimental results introduced in this study should become useful in the design of photochemical electrodes for water splitting and dye-sensitized wet solar cells, and also in the synthesis of photocatalytic powders for purifying water and gases.

5. Conclusions

We have investigated the charge flow through heterojunction, which consists of two semiconductors possessing the equivalent energies of the conduction band edges as well as the valence band edges. The photobleaching of methylene blue aqueous solution with dispersed $(Sr_{0.95}La_{0.05})TiO_{3+\delta}$–$TiO_2$ composite powders was investigated under unfiltered irradiation and visible light irradiation with $\lambda > 420$ nm of Xe discharge.

(1) Under the unfiltered irradiation, the photobleaching smoothly proceeded similarly to that using TiO_2 alone. Under the visible light irradiation, the photobleaching rate was several times larger than that using TiO_2 alone. The absorbance spectrum obtained using the composite powder differed significantly from that using TiO_2 alone. Furthermore, the strong adsorption of methylene blue ions on the composite powder surface was observed.

(2) The results have implied that a monotonic and large energy band bending appeared in a part of $(Sr_{0.95}La_{0.05})TiO_{3+\delta}$ and throughout the TiO_2 layer dipped in aqueous solution. This comes from the fact that the Fermi level of $(Sr_{1-x}La_x)TiO_{3+\delta}$ is sufficiently more negative than that of n-type TiO_2. The difference in the Fermi levels yields an uphill band bending toward TiO_2 in the region of heterogeneous micro-junctions, where no energy steps and spiks exist at the junction interface. This should be useful in the design of photochemical electrodes for water splitting and dye-sensitized wet solar cell.

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