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論　文　名	Investigations on the Preparation of Visible Light-responsive TiO_2 Thin Film Photocatalysts and Their Application to the Evolution of H_2 from pure H_2O and Aqueous Solutions Involving Organic Compounds (可視光応答型の二酸化チタン薄膜光触媒の調製とその水や有機化合物を溶解した水溶液からの光触媒水素発生への応用に関する研究)
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論文要旨

The development of artificial photosynthesis to produce renewable energy and other green energy materials is a major challenge to mankind. Efficient use of the freely available resource of solar energy by its conversion into electricity as well as clean chemical energy will be significant in reducing our dependence on fossil fuels. TiO_2 is one of the most popular oxide materials for its many applications and potential use in a variety of technologies where surface chemistry is critical, including photocatalysis. Recently, TiO_2 has been widely studied as a key component of photocatalysis in water splitting reaction. The main objective of this study was to modify and develop new TiO_2-based photocatalysts that allow the efficient absorption of visible light, thus, enabling such modified TiO_2 to initiate various desired reactions effectively even under visible or solar light irradiation.

Chapter 1 summarized the various studies detailed in this thesis. In Chapter 2, the preparation methods used to develop the TiO_2 thin films were discussed. Among these, sputtering methods have several advantages and, in this study, TiO_2 thin films were deposited by a radio-frequency magnetron sputtering (RF-MS). The films were deposited using a stoichiometric TiO_2 target sputtered in pure Ar at different pressures. The aim of this study was to investigate the effect of the deposition conditions on the structural and photocatalytic properties of the thin films before and after heat treatment. As is shown in the studies, the crystalline phase of the TiO_2 catalysts is an important factor that determines its activity. The influence of the substrate temperatures on the photocatalytic activity of the TiO_2 thin films was also investigated. The main influence of temperature was found to affect the crystallinity of TiO_2.

Reducing the pressure was found to decrease the total sputtering time for a specified thickness. In this Chapter, the design of optimized Vis-TiO_2 thin films for the separate production of H_2 and O_2 was also discussed. Optimizing of the photocatalytic activity of Vis-TiO_2 thin films prepared by a RF magnetron sputtering (RF-MS) method by controlling the various parameters such as sputtering pressure and target-to-substrate distance $D_{T\text{-}S}$ was investigated. It was shown through different characterization experiments that the optimal sputtering pressure was 2.0 Pa. At this pressure, the highest activity for the Vis-TiO_2 thin films could be attained. When the sputtering pressure was fixed at 2.0 Pa and the target-to-substrate distance was $D_{T\text{-}S}$=75 mm, the best results were obtained.

It was also found that chemical etching of the Vis-TiO_2 thin films with HF solution remarkably enhanced their photocatalytic activity. Such optimized HF-Vis-TiO_2/Ti thin film electrodes exhibited a significant increase in their photocurrent under UV and visible light irradiation as compared to untreated Vis-TiO_2/Ti. SEM and BET surface measurements revealed that the surface roughness increased and the interspace between the columnar TiO_2 crystallites were extended by HF treatment, indicating that HF-Vis-TiO_2/Ti has a shorter diffusion length for the photoformed holes to reach the solid–liquid interfaces than untreated Vis-TiO_2/Ti. The donor densities of Vis-TiO_2/Ti were found to increase after HF treatment, indicating that the photogenerated electrons of HF (60)-Vis-TiO_2/Ti can reach the TiO_2 substrate interface more easily than Vis-TiO_2/Ti due to its higher conductivity. Moreover, the chemical etching of Vis-TiO_2 by HF solution was found to lead a remarkable increase in the separate evolution of H_2 and O_2 under visible light irradiation ($\lambda \geq 450$ nm). Thus, HF (60)-Vis-TiO_2/Ti/Pt thin film photocatalysts were found to be successful in realizing the stoichiometric separate evolution of H_2 and O_2.

Chapter 3 dealt with the post heat treatment of visible light-responsive TiO_2 thin film photocatalysts (Vis-TiO_2) prepared on Ti metal foil (Vis-TiO_2/Ti) or ITO glass (Vis-TiO_2/ITO) substrates by the RF magnetron sputtering (RF-MS). The UV–Vis spectra as well as photoelectrochemical performance of Vis-TiO_2 were affected by various heat treatments such as calcination in air or ammonia. Calcination treatment in NH_3 (1.0×10^4 Pa, 673 K) was found to be particularly effective in increasing the visible light absorption of Vis-TiO_2 as well as in enhancing its photoelectrochemical performance and photocatalytic activity. The Vis-TiO_2 thin film photocatalyst was prepared by the RF-MS method on one side and nanoparticles of Pt were deposited on the opposite side of a Ti metal foil substrate (Vis-TiO_2/Ti/Pt). The separate evolution of H_2 and O_2 from H_2O could be successfully achieved by using an H-shape glass cell consisting of two aqueous phases separated by Vis-TiO_2/Ti/Pt photocatalytic device and a proton-exchange membrane. It was found that the rate of the separate evolution of H_2 and O_2 was also dramatically enhanced by the calcination treatment of Vis-TiO_2 photocatalyst in ammonia.

Chapter 4 dealt with the preparation of double-layered TiO_2 thin film in order to improve the reactivity of TiO_2 thin film photocatalyst. A double-layered visible light-responsive TiO_2 thin film photocatalyst was prepared on a Ti foil substrate by a RF-MS method. The produced DL-TiO_2/Ti consisted of a UV light-responsive TiO_2 thin film (UV-TiO_2) prepared on a Ti foil substrate which a visible light-responsive TiO_2 thin film (Vis-TiO_2) was prepared on it. DL-TiO_2/Ti exhibited higher photoelectrochemical and photocatalytic performance under both UV and visible light irradiation than a single-layered Vis-TiO_2 thin film photocatalyst prepared on a Ti foil substrate. The optimal thickness of the UV-TiO_2 thin film of DL-TiO_2/Ti was found to be about 100nm. Expanding on this work, a novel double-layered TiO_2 thin film device, DL-TiO_2/Ti/Pt, was also prepared by a RF-MS method where DL-TiO_2 was prepared on one side and Pt was deposited on the other side of a Ti foil substrate. The separate evolution of H_2 and O_2 from H_2O was successfully achieved by using an H-type glass cell consisting of two aqueous phases separated by the DL-TiO_2/Ti/Pt and a proton-exchange membrane.

In Chapter 5, two aspects, the production of visible light responsive TiO_2 thin films and their characterizations were focused. TiO_2 thin films were fabricated on quartz substrates under similar conditions. The main part of this Chapter dealt with the photocatalytic degradation of organic contaminants which were found in landfill leachate and methylene blue by utilizing the Vis-TiO_2 thin films. In this study, the changes in the concentrations of COD and TOC as well as UV absorbance of the water involving contaminants at a given wavelength were investigated. The results clearly showed that the novel Vis-TiO_2 thin film photocatalyst led to a remarkably decrease in the concentration of contaminants under solar light irradiation.

In Chapter 6, the Vis-TiO_2 thin films developed in Chapter 2 were also applied in developing sandwich-type dye-sensitized solar cells (DSSC). Two kinds of sandwich-type dye-sensitized solar cells, $DSSC_{Vis}$ and $DSSC_{UV}$, were fabricated using Vis-TiO_2 ($DSSC_{Vis}$) and UV-TiO_2 electrodes ($DSSC_{UV}$), and their photovoltaic performances were investigated under illumination with an AM-1.5 solar simulator lamp (100 $mWcm^{-2}$). $DSSC_{Vis}$ exhibited remarkably higher incident photon-to-electron conversion efficiency (IPCE) than $DSSC_{UV}$. Furthermore, it was found that the optimized solar-to-electric energy conversion efficiencies (η) reached 2.6 % for $DSSC_{Vis}$. UV-Vis, SEM and photoelectrochemical investigations on $DSSC_{Vis}$ and $DSSC_{UV}$ revealed that the unique film morphology as well as band structure of Vis-TiO_2 thin films play an important role in realizing the high photovoltaic performance of $DSSC_{Vis}$.

Chapter 7 presented the results of the evolution of H_2 from an aqueous solution involving various light hydrogen-rich compounds such as various alcohols, hydrocarbons, hydrazine and ammonia. As NH_3 contains no carbon, it is a promising source of hydrogen. Investigations on photocatalytic H_2 evolution using different concentrations of NH_3 clearly showed that the production of hydrogen from ammonia aqueous solution. Thus the present research unveiled that the photocatalytic hydrogen production from ammonia aqueous solution is a promising process for low-cost, low-temperature, high-purity *in situ* hydrogen production. Using higher concentrations of ammonia in aqueous solution led to a reasonably high production of hydrogen, and the best result was obtained at 28%W of ammonia solution.

Finally, the results and conclusions of the core topics of Chapters 2 to 7 were summarized in the final Chapter 8. This Chapter also presented several topics for further studies in unraveling the mechanisms behind the photocatalytic reactions as well as in the development of new photocatalysts with high performance and functionality.

審査結果の要旨

本論文は、RF マグネトロンスパッタ法により可視光応答型酸化チタン薄膜光触媒（Vis-TiO_2）を構築し、各種成膜条件の最適化による光触媒活性の高効率化を図るとともに、それを光触媒とする可視光照射下での水や有機化合物水溶液からの水素生成反応の探索を目的として行った研究をまとめたものである。また、本論文では、色素増感太陽電池の電極材料に Vis-TiO_2を応用する研究も遂行しており、次のような成果を得ている。

(1)RF マグネトロンスパッタ法における基板温度(T)、スパッタガス圧(P)、ターゲット-基板間距離(D_{t-s})などの各種成膜条件が Vis-TiO_2の活性に及ぼす影響について検討し、T=873 K，P=2.0 Pa，D_{t-s}=75 mm の場合に最も高い可視光吸収と光触媒活性が得られることを見いだしている。さらに、HF 水溶液により Vis-TiO_2を化学的にエッチングすることで、H 型セルを用いた太陽光照射下での水からの水素と酸素の分離生成効率が向上することを明らかにしている。

(2)アンモニアガス中での焼成処理により、Vis-TiO_2の光電気化学特性や光触媒活性が向上することを見いだしている。また、各種分光測定により、アンモニアガス中での焼成処理により Vis-TiO_2中の Ti^{3+}種が減少し、電子と正孔の再結合が抑制されるため光触媒活性が向上することを明らかにしている。

(3) Ti 基板上に紫外光応答型薄膜光触媒を成膜し、その上に Vis-TiO_2を成膜した積層型薄膜光触媒(DL-TiO_2/Ti)が、一層型の Vis-TiO_2/Ti より高い光触媒活性を示すことを見いだすとともに、その高い活性が Ti 基板から電解質溶液への逆電子移動の抑制に起因することを明らかにしている。

(4) Vis-TiO_2を電極とする高効率な色素増感太陽電池($DSSC_{Vis}$)の構築に成功するとともに、Vis-TiO_2の伝道帯の下端が通常の TiO_2より正に位置しており、色素から Vis-TiO_2への効率よい電子注入が可能となるため $DSSC_{Vis}$の特性が向上することを各種光電気化学測定により明らかにしている。

以上の諸成果は、可視光応答型酸化チタン薄膜光触媒の創製とその高効率化、および高効率な色素増感太陽電池の構築に貢献すること大である。また、申請者が自立して研究活動を行うに必要な能力と学識を有することを証したものである。