論文 / 著書情報
Article / Book Information

題目(和文)	ヘテロポリ酸/ブルッカイト複合薄膜の作製とその光触媒活性
Title(English)	Preparation and photocatalytic activity of heteropolyacid/brookite hybrid films
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出典(和文)	学位:博士（工学）, 学位授与機関:東京工業大学, 報告番号:甲第9616号, 授与年月日:2014年9月25日, 学位の種別:課程博士, 審査員:中島　章,坂井　悦郎,生駒　俊之,宮内　雅浩,松下　祥子
Citation(English)	Degree:, Conferring organization: Tokyo Institute of Technology, Report number:甲第9616号, Conferred date:2014/9/25, Degree Type:Course doctor, Examiner:,,,,
学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

（博士課程）
Doctoral Program

論 文 要 旨

THESIS SUMMARY

専攻： Department of	材料工学 専攻	申請学位（専攻分野）： Academic Degree Requested	博士 Doctor of （工学）
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要旨（英文800語程度）
Thesis Summary（approx.800 English Words ）

During UV illumination, Titanium dioxide (TiO_2) generates electron-hole pair which is useful for water and air purification. Moreover, photoinduced hydrophilicity (PIH) also happens on TiO_2 UV-illuminating surface. However, some limitations of its quantum yields remain because of its electron hole recombination and its low Fermi level for O_2 reductions. Inhibition of this electron–hole recombination is an effective approach to improving TiO_2 photocatalytic activity. Various investigations of this concept have been conducted, such as Pt loading, hybridization of other oxides, and a Z-scheme design.

Heteropolyacids (HPAs) are a subclass in a family of polyoxometalates (POMs), which are clusters of metal oxides that have a well-defined structure. These are metal oxide frameworks called polyanions that include heteroanions. The total charge is balanced by counter-cations. They are not only acid catalysts, but also photocatalytic materials. Materials of this group enhance the photocatalytic activity of TiO_2 by a Z-scheme. Initially, the HPA (aq.)/TiO_2(s) system was mainly studied.

Recently, Yanagida prepared transparent HPA/TiO_2 hybrid films using layer-by-layer (LBL) process with a commercial anatase sol. The effect of heteroatom and polyatom on the entire photocatalytic decomposition of the hybrid films was investigated. However, the effect of TiO_2 species and the film structure have not been studied. Moreover, wettability conversion including hydrophilicizing process and subsequent sustainability of the hydrophilicity of these hybrid films has not well incestigated thus far. In the present study, we investigated these topics systematically using brookite sol, and obtained a new understanding on the surface wettability control.

In the 1st chapter, recent studies for titanium dioxide (TiO_2), heteropolyacids (HPAs) and HPAs/ TiO_2 hybrid material were reviewed. Then the objective and strategy for this research were stated.

In the 2nd chapter, transparent 12-Tungstophosphoric acid (PW_{12})/brookite hybrid films were prepared via LBL processes on a quartz substrate. Their photocatalytic activities were evaluated using gaseous 2-propanol (IPA) decomposition. Pure brookite film showed higher photocatalytic activity than the pure PW_{12} one; the combination of PW_{12} to brookite increased the photocatalytic activity. Different from the previous HPAs/anatase, the secondary excitation for these hybrid films play no important role because a sufficient number of generated electrons transferred directly from brookite to LUMO of PW_{12}. The electron

scavenger effect of PW_{12} against brookite under UV illumination plays an important role in photocatalytic decomposition activity improvement. The degree of improvement depends on the stacking order in the films. Their photocatalytic activity was the highest when PW_{12} was arranged on the film's topmost surface.

In the 3rd chapter, a comparative study of photocatalytic decomposition activity and photoinduced hydrophilicity for the transparent PW_{12}/brookite hybrid films was conducted using gaseous IPA decomposition and sessile drop method. Heat-treatment at 300^{o}C was conducted in the film processing to decrease the solubility of PW_{12} in water. After heat-treatment, Kegging-type structure of PW_{12} was still retained. The TTP film (PW_{12} was deposited onto the brookite bilayer) exhibited better photocatalytic activity than that of the TT film (pure brookite control film). Moreover, the TTP film provided a higher hydrophilicizing rate under UV illumination, and provided better sustainability of the hydrophilicity in the dark than the TT film did. The sustainability depended on the storage atmosphere. The hydrophobicizing rate on the TTP was slow in the oxygen deficient atmosphere. These results suggest that reduced PW_{12} enhanced water adsorption on the film.

In the 4th chapter, two tungsten-based Keggin-type heteropolyacids (PW_{12}: ($[PW_{12}O_{40}]^{3-}$) and SiW_{12}: ($[SiW_{12}O_{40}]^{4-}$)) were hybridized with brookite-type TiO_2. Then photocatalytic decomposition activity, photoinduced hydrophilicity, and sustainability of the hydrophilicity in the dark were evaluated using IPA decomposition and sessile drop method. Both hybrid films exhibited higher photocatalytic decomposition activity and had higher photoinduced hydrophilicizing rates than the pure brookite film under UV illumination. The PW_{12}/TiO_2 film exhibited better photocatalytic performance than the SiW_{12}/TiO_2 film did. Atmosphere dependence, XPS analysis, and electrochemical experiments indicated the cause of these two films' different levels of sustainability of hydrophilicity to be differences in their electron storage capability. Results show that the electron scavenger capability and reoxidation efficiency of the heteropolyacid are key factors affecting the overall performance of wettability conversion of this hybrid film system before and after UV illumination.

In the 5th chapter, overall content from chapter 2, 3 and 4 were summarized. There are two main successes for this research. First, PW_{12} on TiO_2 not only acts as electron scavenger but also enable multi-electron reduction by O_2. Second, during UV illumination, PW_{12} collects electrons from TiO_2. Then, these collected electrons polarize the total film surface after stopping illumination, which enhances wettability of the film. Therefore, the combination of PW_{12} to TiO_2 can improve both photocatalytic decomposition activity and wettability in the same time, which superior to the common photocatalyst such as Pt-loaded TiO_2 or SiO_2-TiO_2.