Nanocrystalline $CaZrTi_2O_7$ Photocatalyst Prepared by a Polymerizable Complex Method in the Presence of Cs_2CO_3 Flux for Water Splitting

Yugo Miseki, Kenji Saito, and Akihiko Kudo*
Department of Applied Chemistry, Faculty of Science, Tokyo University of Science,
1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601

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Photocatalytic and photophysical properties of $CaZrTi_2O_7$ were investigated. When the $CaZrTi_2O_7$ powder was prepared by a polymerizable complex method in the presence of Cs_2CO_3 flux, powder with high crystallinity and 100–300 nm of a primary particle size was obtained. The band gap of the $CaZrTi_2O_7$ powder was 3.6 eV. It showed a broad photoluminescence band around 580 nm at 77 K. Activated $NiO/CaZrTi_2O_7$ showed photocatalytic activity for water splitting into H_2 and O_2 under UV irradiation.

Water splitting has been paid attention as an ideal hydrogen production method. Many metal oxide photocatalysts that respond to UV, and some metal oxynitride, nitride, and Z-scheme type photocatalysts that respond to visible light have been developed during this decade.[1] However, the present efficiency is not satisfying for the practical use. Therefore, the construction of a photocatalyst library and clarification of factors affecting photocatalytic abilities are important in order to establish a guiding principle for design of a photocatalyst. Most oxide photocatalysts consisting of metal cations with d^0 configuration are composed of MO_6 octahedral units as seen in perovskite compounds.[2] The present authors have reported that $Cs_2Nb_4O_{11}$ consisting of NbO_4 tetrahedral and NbO_6 octahedral units shows relatively high photocatalytic activity for water splitting among niobate photocatalysts.[3] This result motivates us to investigate photocatalytic properties of metal oxide materials consisting of some kinds of polyhedra. $CaZrTi_2O_7$ has anion-defect-type fluorite structure with TiO_4 tetrahedra, TiO_6 octahedra, and ZrO_7 decahedra.[4] Therefore, it will be an interesting material as a photocatalyst for water splitting. It is reported that $CaZrTi_2O_7$ is prepared by a solid-state reaction using oxide starting materials at 1723 K.[4,5] Flux and polymerizable complex methods give highly crystalline particles at relatively low temperature compared with solid-state reaction for ceramics syntheses.[6]

In the present study, low-temperature synthesis of $CaZrTi_2O_7$ was explored by the polymerizable complex method (PC method). Effects of Cs_2CO_3 flux on the condition of prepared $CaZrTi_2O_7$ powder were examined. Photocatalytic and photophysical properties of the $CaZrTi_2O_7$ powder were investigated.

$CaCO_3$ (Kanto Chemical; 99%), $Ti(OC_4H_9)_4$ (Kanto Chemical; 97%), $ZrO(NO_3)_2\cdot 2H_2O$ (Kanto Chemical; 99%), citric acid (Sigma Aldrich Japan; 99.5%), and propylene glycol (Kanto Chemical; 99.0%) were employed as starting materials for a PC method according to a previous report.[6] Cs_2CO_3 (Kojundo Chemical; 99.9%) that functions as a flux reagent at calcination of precursor was added, if necessary. Metal compounds and a citric acid were dissolved in a mixed solvent of methanol and propylene glycol. The mixed solution was aged at 353 K for 2 h. At this stage, sol containing citric complexes was formed. The sol was dehydrated to form gel by polymerization at 393 K for 12 h. A precursor was obtained by calcination of the gel containing a citric acid using a mantle heater. $CaZrTi_2O_7$ was prepared by calcination of the precursor at 1173–1473 K for 10 h. The Cs_2CO_3 flux was washed out with water after the preparation. Phase purity of the obtained powders was confirmed by X-ray diffraction (Rigaku; MiniFlex). NiO cocatalysts were loaded by an impregnation method from an aqueous $Ni(NO_3)_2$ solution. The $CaZrTi_2O_7$ powder impregnated with $Ni(NO_3)_2$ was calcined at 543 K for 1 h in air. Pretreatment of reduction with 200 Torr of H_2 at 773 K for 2 h followed by oxidation with 100 Torr of O_2 at 373–573 K for 1 h was carried out for NiO-loaded photocatalysts as activation treatment.[7] Diffuse reflection spectra were obtained using a UV–vis–NIR spectrometer (Jasco; UbestV-570), converting from reflectance to absorbance modes by the Kubelka–Munk method. Photoluminescence spectra of $CaZrTi_2O_7$ were measured using a fluorospectrometer (HORIBA JOBIN YVON; SPEX Fluorolog-3). The photocatalyst power was observed by a scanning electron microscope (SEM, JEOL JSM-6700F). Water-splitting reactions were carried out in a gas-closed circulation system. $CaZrTi_2O_7$ (0.5 g) was dispersed in pure water or an aqueous NaOH solution (380 mL) by a magnetic stirrer in an inner irradiation reaction cell made of quartz equipped with a 400-W high-pressure mercury lamp (SEN: HL400EH-5). The amounts of evolved H_2 and O_2 were determined using on-line gas chromatography (Shimadzu; MS-5A column, TCD, Ar carrier). Apparent quantum yields at 270 nm were determined according to a previous report.[1]

A single phase of $CaZrTi_2O_7$ was obtained by a PC method at 1173 K while impurity phases were formed in addition to the $CaZrTi_2O_7$ phase by a solid-state reaction even at 1623 K. The effect of Cs_2CO_3 flux on the preparation of $CaZrTi_2O_7$ powder by PC method was examined by a scanning electron microscope as shown in Figure 1. Plate-like powder with a lot of boundary and several tens of µm in size was obtained in the absence of

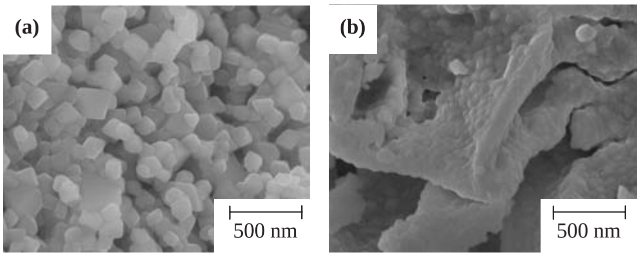

Figure 1. Scanning electron microscope photographs of $CaZrTi_2O_7$ prepared by a PC method (a) with and (b) without Cs_2CO_3 flux (1273 K, 10 h).

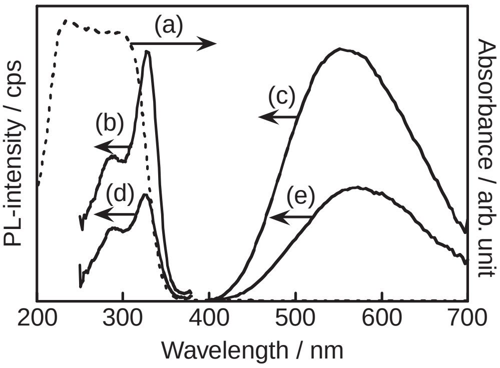

Figure 2. (a) A diffuse reflection spectrum of $CaZrTi_2O_7$ at room temperature, (b) exciation and (c) emission spectra at 100 K of $CaZrTi_2O_7$ prepared with Cs_2CO_3 flux, (d) excitation and (e) emission spectra at 100 K of $CaZrTi_2O_7$ prepared without Cs_2CO_3 flux.

the Cs_2CO_3 flux. In contrast, in the presence of the Cs_2CO_3 flux, highly crystalline powder with 100–300 nm in primary particle size was prepared. It was confirmed by EDS that no Cs was included in the particles. This result indicates that the Cs_2CO_3 flux is effective for preparation of nano-crystalline metal oxide powder. The particle size of metal oxide powder prepared in the presence of a flux reagent is usually larger than that in the absence of a flux reagent because of well crystal growth. Therefore, this result is novel and important from the viewpoint of a preparation method.

Figure 2 shows a diffuse reflection spectrum at room temperature and photoluminescence at 100 K of $CaZrTi_2O_7$ powder. The band gap was 3.6 eV. The $CaZrTi_2O_7$ powder showed a broad photoluminescence band around 580 nm. The excitation spectrum agreed with the diffuse reflection spectrum indicating that the photoluminescence is due to the band gap excitation. The intensity of the photoluminescence of $CaZrTi_2O_7$ powder prepared with Cs_2CO_3 flux was larger than that prepared without the Cs_2CO_3 flux. The nanocrystalline powder would affect the enhanced photoluminescence property. Two excitation bands were observed for excitation spectra. This result suggests that there are some excited states due to some kinds of polyhedra in $CaZrTi_2O_7$.

Table 1 shows water splitting over $CaZrTi_2O_7$ powder prepared by a PC method. The preparation conditions, amount of NiO cocatalyst, and activation conditions were optimized for each photocatalyst. The photocatalytic activity of the $CaZrTi_2O_7$ powder without a NiO cocatalyst was negligible. Activated $NiO_x/CaZrTi_2O_7$ photocatalyst showed activity for water splitting. It is reported that pH control improves activities for several photocatalysts.[8] The $NiO_x/CaZrTi_2O_7$ photocatalyst gave the highest activity at pH 12. The photocatalytic activity of $CaZrTi_2O_7$ prepared with Cs_2CO_3 flux was higher than that prepared without Cs_2CO_3 flux. Photogenerated electrons and holes have to migrate to the surface in the photocatalytic process. Therefore, the nanocrystalline powder of the $CaZrTi_2O_7$ photocatalyst prepared with Cs_2CO_3 flux is advantageous for shortening the distance that the electrons and holes have to migrate resulting in high activity. When a Pyrex reaction cell was used the activity was very low. This result indicates that the higher energy excitation state as observed in Figure 2 mainly contributes to the appearance of the photocatalytic activity. A similar result is obtained for a CeO_2 photocatalyst.[9] Figure 3 shows water splitting over an optimized $NiO_x/CaZrTi_2O_7$ photocatalyst. 1.5 and 0.75 mmol of H_2 and O_2 were obtained at 10 h, respectively. The turnover number of reacted electrons to molar quantity of photocatalyst was 2.2 at 10 h. These results clearly indicate that the water splitting proceeded photocatalytically. The quantum yield at 270 nm was 0.2%.

In conclusion, the Cs_2CO_3 flux for calcination of a precursor prepared by a PC method was effective for preparation of nanocrystalline metal oxide powder. The $CaZrTi_2O_7$ powder prepared with the Cs_2CO_3 flux gave more intensive photoluminescence and higher photocatalytic activity for water splitting than that prepared without the Cs_2CO_3 flux.

Table 1. Photocatalytic water splitting over $CaZrTi_2O_7$ prepared by a PC method[a]

Cs_2CO_3 flux	Reactant	S.A. /$m^2\ g^{-1}$	NiO_x[b] /wt %	Activity /$\mu mol\ h^{-1}$	
				H_2	O_2
No	Water	3.9	None	2	0
No	Water	3.9	2.0	51	23
No	NaOH aq (pH 12)	3.9	2.0	76	36
Yes	NaOH aq (pH 12)	10.1	2.0	211	100
Yes	NaOH aq (pH 12)	10.1	2.0	0.7	0.2

[a] Catalyst (0.5 g), aqueous solution (380 mL), inner irradiation cell made of quartz, 400-W high-pressure mercury lamp. [b] Pretreated by H_2 reduction at 773 K for 2 h and subsequent O_2 oxidation at 473 K for 1 h. [c] A Pyrex reaction cell was used.

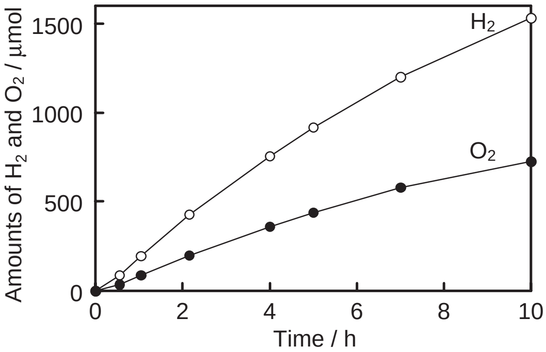

Figure 3. Photocatalytic water splitting over pretreated NiO_x (2.0 wt %)/$CaZrTi_2O_7$. Catalyst (0.5 g), pure water (380 mL), inner irradiation cell made of quartz, 400-W high-pressure mercury lamp.

References and Notes

1 A. Kudo, Y. Miseki, *Chem. Soc. Rev.* **2009**, and references therein. doi: 10.1039/B800489G.
2 F. E. Osterloh, *Chem. Mater.* **2008**, *20*, 35, and references therein.
3 Y. Miseki, H. Kato, A. Kudo, *Chem. Lett.* **2005**, *34*, 54.
4 H. J. Rossell, *Nature* **1980**, *283*, 282.
5 H. J. Rossell, *J. Solid State Chem.* **1992**, *99*, 52.
6 M. Kakihana, K. Domen, *MRS Bull.* **2000**, *25*, 27.
7 K. Domen, A. Kudo, T. Onishi, N. Kosugi, H. Kuroda, *J. Phys. Chem.* **1986**, *90*, 292.
8 T. Takata, Y. Furumi, K. Shinohara, A. Tanaka, M. Hara, J. N. Kondo, K. Domen, *Chem. Mater.* **1997**, *9*, 1063.
9 H. Kadowaki, N. Saito, H. Nishiyama, Y. Inoue, *Chem. Lett.* **2007**, *36*, 440.

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