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Effects of Redox Potential of Metallophthalocyanine Dye on Photocatalytic Activity of $KTa(Zr)O_3$ for Water Splitting

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Photocatalytic activity of dye-modified $KTaO_3$ correlated with the first redox potential of phthalocyanines. It was found that the most effective dye for improving water-spritting activity was Cr–phthalocyanine (Cr–Pc) with a redox potential of −0.8 V vs. SCE.

Photocatalysts for splitting H_2O into H_2 and O_2 have been studied for the purpose of H_2 production with solar energy. To date, the photocatalytic activity of various oxides, sulfides, and the other inorganic compounds has been investigated for water splitting, and among them, Ta oxide compounds have been reported as highly active photocatalysts for decomposition of water.[1,2] In our previous study, it was found that the photocatalytic activity of Zr-doped $KTaO_3$, which is a typical perovskite oxide, was improved by coating with various porphyrin dyes.[3] Porphyrinoids are known as organic semiconductor and have been studied for conversion of light energy to electric or chemical energy.[4,5] In this study, dependency of the photocatalytic activity on the redox potential of metallophthalocyanines was investigated to reveal the effects of charge-transfer efficiency from $KTaO_3$ to dye for water-splitting activity.

Details of preparation method for dye-modified $KTa_{0.92}Zr_{0.08}O_3$ ($KTa(Zr)O_3$) photocatalyst are reported in a previous paper from these laboratories.[3] Pt cocatalyst was loaded on hydrophobic metallophthalocyanines which were adsorbed on the surface of $KTa(Zr)O_3$. Commercial metal-free phthalocyanine was used without further purification in this study. Metallophthalocyanines were prepared by refluxing the appropriate metal chloride in pyridine solvent with metal-free phthalocyanine. After washing with pure water, the intercalation of central metal to phthalocyanine was confirmed by using energy dispersive X-ray fluorescence spectrometry (Shimadzu Corp., μEDX-1200). The photocatalytic decomposition of water was carried out in a quartz reactor with a conventional closed circulating system. The light source used was a 500 W Xe lamp (Ushio Inc., SX-UI500XQ) without glass filter. The amount of formed gases was measured with a TCD gas chromatograph (Shimadzu Co., GC-8A), which was connected to a closed circulating system and vacuum line.

Photocatalytic water splitting on $Pt/Co–Pc/KTa(Zr)O_3$ catalyst was performed using a Xe lamp as a light source (Supporting Information).[12] After the immediate light irradiation, linear formation of H_2 and O_2 was observed with a negligible amount of N_2 formation and the H_2/O_2 ratio was almost 2. Over 30 h, the total amounts of H_2 and O_2 formed were 275 and 126 µmol, respectively. In the case of complete oxidation, a Co–Pc molecule consumes almost 45 O_2 molecules. Since the amount of evolved H_2 was over 78.9 µmol, which was calculated when Co–Pc was completely oxidized as sacrificial reagent, it appears that Co–Pc worked as a promoter. In fact, stability of organic dye was also studied. Figure 1 shows UV–vis spectra of $Pt/Co–Pc/KTa(Zr)O_3$ before and after measurement. It was observed that the absorption frequency of the $KTa(Zr)O_3$ catalyst was expanded to the visible light region by modification with Co–Pc. Broad absorption peaks assigned to the Q-band absorption of Co–Pc were observed at 600 and 680 nm. Although Q-band absorbance decreased slightly after photoirradiation for 6 h, almost the same spectra were observed after an additional 30-h reaction. Loading of Co–Pc was determined to be 0.28 wt% after 30-h photoirradiation. Therefore, it is suggested that decreases in absorption peaks may not be caused by decomposition but elution of dye, and Co–Pc which remained on the surface of $KTaO_3$ contributed to the water-splitting reaction without decomposition.

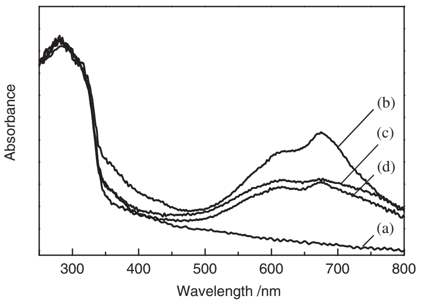

Figure 1. UV–vis spectra of (a) $Pt/KTa(Zr)O_3$, (b) $Pt/Co–Pc/KTa(Zr)O_3$ before reaction, $Pt/Co–Pc/KTa(Zr)O_3$ after photoirradiation for (c) 6 h and (d) 30 h.

Phthalocyanine is able to coordinate various metal cations, and it is well known that various properties such as electrical conductivity and optical and electrochemical properties can be modified by the central metal.[6,7] Table 1 shows the effects of central metal cation on the water-splitting activity of $Pt/M–Pc/KTaO_3$ photocatalysts. Gas formation rates of H_2 and O_2 vary significantly with central metal in spite of the same ligand. Photocatalytic activity was improved by using Pc coordinated with rare earth metal (La, Sm, and Pr). Furthermore, Pt-loaded $KTaO_3$ modified with Pc, which was coordinated with trivalent metal cation, tends to achieve a high photocatalytic activity, and $Pt/Cr–Pc/KTaO_3$ photocatalyst exhibited the highest H_2 and O_2 formation rates among the examined catalysts. Although water splitting was achieved on the dye-modified $KTaO_3$ photocatalysts without wavelength filtering, the reaction cannot be observed under Xe lamp irradiation with a UV cut-off filter ($\lambda > 385$ nm). This result clearly shows that the excitation of $KTaO_3$ was necessary to achieve water splitting on dye-modified $KTaO_3$ photocatalyst.

Table 1. Photocatalytic activity for water splitting on Pt/KTa(Zr)O_3 modified with M–phthalocyanine[a]

Central metal (M)	Amount of dye/μmol	Formation rate/μmol g_{cat}^{-1} h^{-1}	
		H_2	O_2
Cr	0.89	52.0	25.1
La	0.77	47.8	19.9
Fe	0.88	38.6	Trace
Sm	0.75	36.5	16.0
Pr	0.77	35.7	15.0
Mn	0.88	32.6	Trace
Co	0.87	22.3	9.3
Ti	0.89	20.7	2.1
Ni	0.88	12.5	1.9
V	0.89	12.0	Trace
None	—	1.9	0.7

[a] Catalyst: Pt(0.1 wt %)/M–phthalocyanine(0.5 wt %)/$K_{1.15}Ta_{0.92}Zr_{0.08}O_3$, Light source: 500 W Xe lamp without cut-off filter, pH: 11.

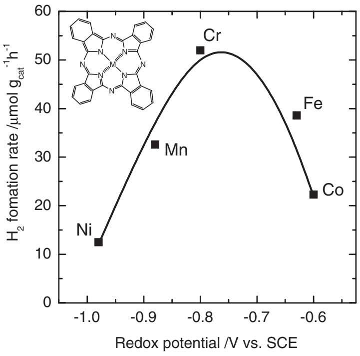

Figure 2. Relationship between redox potential of M–Pc (M: Ni, Mn, Cr, Fe, and Co)[8] and H_2 formation rate.

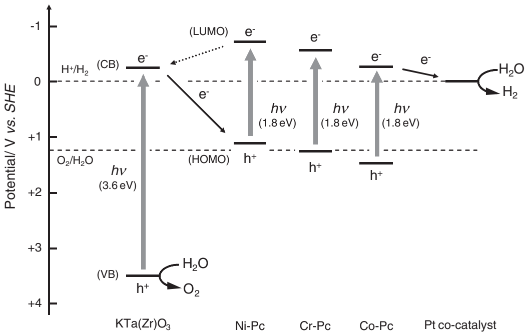

Figure 3. Schematic mechanism for the photocatalytic splitting of water into H_2 and O_2 on dye-modified KTa(Zr)O_3.

For understanding central cation effects, relationships between the redox properties of Pc and photocatalytic activity were studied. Figure 2 shows the H_2 formation rate as a function of the redox potential of M–Pc (M: Ni, Mn, Cr, Fe, and Co) reported by Zagal et al.[8] A strong dependency is observed between the H_2 formation rate and the redox potential. High H_2 formation rate is obtained for dye with a redox potential around −0.8 V vs. SCE. This suggests that charge transfer from KTa(Zr)O_3 to M–Pc occurs, and an optimum redox level exists for improving photocatalytic activity of $KTaO_3$. Figure 3 shows the estimated HOMO and LUMO levels of KTa(Zr)O_3, M–Pc, and Pt co-catalyst with H_2 and O_2 evolution potential. Band structure of $KTaO_3$ was determined by UV–vis absorption spectra and references,[9] and the band gap of M–Pc was also estimated by the absorption spectra. In our previous study, it was suggested that the charge photoexcited in $KTaO_3$ was transferred to the organic dye followed by photoexciting again, i.e., two-step excitation which is similar to the Z-scheme diagram of photosynthesis in plants.[10] In the case of Co–Pc, the excited level (LUMO level) is almost the same as that of $KTaO_3$, and this may not be high enough for transfer to Pt. In fact, H_2 formation rate was small. In contrast, the LUMO level in Ni–Pc is excessively high, and the back electron transfer from Ni–Pc to $KTaO_3$ is easier, as also suggested for a dye-sensitized solar cell.[11] In the case of dye-modified $KTaO_3$ photocatalyst, it is expected that the electron transfer from dye to $KTaO_3$ leads to the charge recombination resulting in a decrease in photocatalytic activity. Therefore, H_2 formation rate is also smaller on Ni–Pc dye. Since the charge transfer from $KTaO_3$ to dye is feasible and also back donation from dye to $KTaO_3$ is prevented, the optimal band energy level exists for phthalocyanine dye. Consequently, the optimal band level exists in dye which seems to be −0.8 V vs. SCE and so the dependency of central metal in metallophthalocyanine can be explained by the charge-transfer efficiency. This study reveals that the surface modification with M–Pc is an effective method to improve the photocatalytic activity of $KTaO_3$.

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12 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.