Photocatalysis

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Dye-Sensitizer Effects on a Pt/KTa(Zr)O_3 Catalyst for the Photocatalytic Splitting of Water**

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The development of an active catalyst for the photocatalytic decomposition of pure water into H_2 and O_2 is urgently required from an energy-saving viewpoint. Various semiconductor oxides, mainly TiO_2- and Nb-based mixed oxides, have been investigated for this reaction.[1,2] Recently, however, various Ta-based oxides reported by Kato and Kudo et al. have attracted interest as new photocatalytic materials because of their fairly high activity for the photocatalytic splitting of H_2O.[3–5] In addition, Zou et al. have found that Ni-doped $InTaO_4$ can decompose H_2O upon activation with visible light,[6] as can the mixed $SrTiO_3/WO_3$ compound reported by Sayama et al.[7,8] In a previous study we found that Zr-doped $KTaO_3$ exhibits a high activity, splitting H_2O into almost stoichiometric amounts of H_2 and O_2.[9,10] However, these photocatalysts mainly consist of oxide semiconductors combined with a metal or metal oxide such as Pt or NiO. On the other hand, dye-sensitized solar cells are attracting a great deal of interest because of their simple structure and high efficiency.[11,12] In these cells a free electron is excited in the organic dye and passes through a TiO_2 electrode to the counter electrode. Although the structure of these solar cells is simple, a high energy conversion up to 11% can be achieved, and the electron-transfer step resembles that in photocatalysis. Indeed, the application of dye-sensitized solar cells to the photolysis of water has also been reported,[12] therefore a dye-sensitized TiO_2 electrode should also function as a photocatalyst for the splitting of water into H_2 and O_2.

Photocatalysts sensitized by various organic dyes have been investigated, and it has been reported that hydrogen forms under visible-light irradiation of Pt/TiO_2 in the presence of bipyridyl–ruthenium complex, albeit in a small amount.[13,14] However, the splitting of pure water by a dye-sensitized oxide semiconductor has not yet been achieved. This study reports the sensitizing effects of porphyrinoids on the photocatalytic splitting of H_2O into H_2 and O_2 by Pt/KTa(Zr)O_3 and shows that the addition of porphyrinoids to $KTaO_3$ increases the activity of this compound.

Figure 1 shows a TEM image of $K_{0.95}Ta_{0.92}Zr_{0.08}O_3$ coated with tetraphenylporphyrinatochromium(III). The surface of the particle is covered with an amorphous film of the chromium complex. Therefore, the $KTaO_3$-based oxide is encapsulated with the organic dye and good electronic contact between the oxide semiconductor and organic dye seems to have been achieved. The prepared $KTaO_3$ also appears to have good crystallinity since the lattice image is also observed. The UV/Vis spectrum of the prepared catalyst

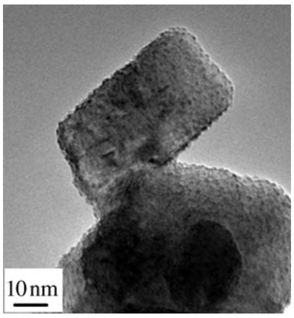

Figure 1. TEM image of Pt-loaded $K_{0.95}Ta_{0.92}Zr_{0.08}O_3$ sensitized by Cr–TPP (rough, thin surface layer).

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is the sum of those of $KTaO_3$ and tetraphenylporphyrinatochromium(III) (Cr–TPP). This also supports the uniform distribution of organic dye on the $KTaO_3$-based oxide.

Table 1 summarizes the photocatalytic activity of the $KTaO_3$ catalyst sensitized by various organic dyes. The observed formation rate of O_2 is almost half that of H_2, and the lowest formation rate of H_2 is 2.1 $\mu mol\,h^{-1}g^{-1}$ for Pt/$K_{0.95}Ta_{0.92}Zr_{0.08}O_3$. It can also be seen that almost no H_2 or O_2 was formed with Pt/cyanocobalamin (vitamin B_{12}) or cyanocobalamin/$KTaO_3$. The formation rate of H_2 and O_2 was greatly increased relative to that for Pt/$K_{0.95}Ta_{0.92}Zr_{0.08}O_3$ by addition of various porphyrinoids. The formation rate of H_2 increases as follows: TPPS < TCPP < Co–TPP ≪ Cr–TPP < TMPyP < cyanocobalamin. Although the rate of formation of H_2 is slightly larger than that of O_2, almost stoichiometric amounts of H_2 and O_2 are formed with respect to H_2O splitting with the various dye-sensitized catalysts studied. In particular, the rate of formation of H_2 is almost twice as large as that of O_2 on Cr–TPP-sensitized Pt/$KTaO_3$. The metal cation of the porphyrin complex also has a large influence on the rate of formation of H_2 and O_2, as can be seen by comparing the results for catalysts sensitized with Co–TPP and Cr–TPP. Among the porphyrinoids examined, cyanocobalamin shows the strongest effect on the photocatalytic splitting of water. Although it would be difficult, changing the central cation of cyanocobalamin from Co^{2+} to Cr^{3+} should greatly improve the photocatalytic activity. In any case, the formation rate of H_2 and O_2 with this cyanocobalamin-based catalyst is the highest obtained in this study (575.0 and 280.4 $\mu mol\,g^{-1}h^{-1}$, respectively). Almost no H_2 and O_2 were observed with Pt/cyanocobalamin as the photocatalyst (Table 1), therefore cyanocobalamin is a promoter rather than a photocatalyst. In view of the narrow bandgap of cyanocobalamin, this result is to be expected. A further study examined the dye-sensitizer effects of cyanocobalamin.

Table 1: Photocatalytic splitting of water into H_2 and O_2 by $K_{0.95}Ta_{0.92}Zr_{0.08}O_3$ sensitized by various organic dyes.[a]

Organic dye	Formation rate [$\mu mol\,g^{-1}h^{-1}$] H_2	O_2
Pt/$K_{0.95}Ta_{0.92}Zr_{0.08}O_3$	2.1	0.7
Pt/cyanocobalamin	4.5	trace
Cyanocobalamin/$K_{0.95}Ta_{0.92}Zr_{0.08}O_3$	6.1	0.5
Pt/organic dye/$K_{0.95}Ta_{0.92}Zr_{0.08}O_3$		
Tetraphenylporphine tetrasulfonic acid (TPPS)	376.8	106.0
Tetrakis(4-carboxyphenyl)porphine (TCPP)	404.2	95.6
Zn–TPP dimer[b]	365.2	152.0
Co–phthalocyanine	22.3	9.3
Cr–phthalocyanine	52.0	25.1
Co–tetraphenylporphyrin (Co–TPP)	145.3	44.8
Cr–tetraphenylporphyrin (Cr–TPP)	512.6	257.0
Chlorophyll a	371.5	122.6
Cyanocobalamin	575.0	280.4

[a] Pt was added for all catalysts except for cyanocobalamin/$K_{0.95}Ta_{0.92}Zr_{0.08}O_3$, and the Pt load and the amount of organic dye are 0.2 and 0.8 wt.%, respectively. Photolysis was performed at pH 11. [b] Pentamethylene bis[4-(10,15,20-triphenylporphin-5-yl)benzoate]dizinc(II).

Figure 2 shows the rate of formation of H_2 and O_2 with different amounts of cyanocobalamin added for $K_{0.95}Ta_{0.92}Zr_{0.08}O_3$. It can be seen that the rate of formation of H_2 and O_2 increases upon increasing the amount of cyanocobalamin, with the highest formation rate achieved at 0.6 wt.%. Since the light absorbed by cyanocobalamin cannot reach the central part of the photocatalyst ($KTaO_3$), addition of a large excess of cyanocobalamin only serves to lower the activity of the catalyst. Therefore an optimum cyanocobalamin load was achieved with 0.8 wt.%.

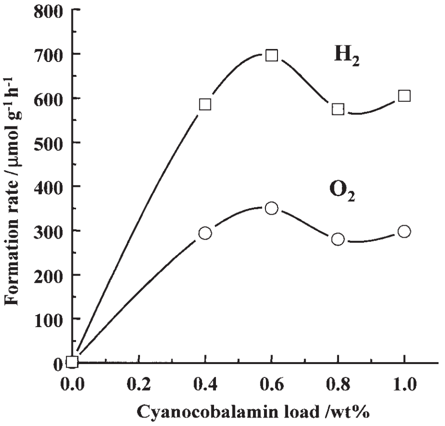

Figure 2. Rate of formation of H_2 and O_2 as a function of amount of added cyanocobalamin for $K_{0.95}Ta_{0.92}Zr_{0.08}O_3$.

Figure 3 shows the amount of H_2 and O_2 formed by Pt/$K_{0.95}Ta_{0.92}Zr_{0.08}O_3$ sensitized by cyanocobalamin after various reaction times. Formation of H_2 and O_2 occurs immediately upon irradiation, and although the rate of formation decreases slightly from the initial rate, it is sustained over the time period examined (9 h). The total amount of H_2 evolved during these 9 hours was 1370 molar times larger than that obtained with cyanocobalamin supported on $KTaO_3$, therefore cyanocobalamin is a promoter rather than

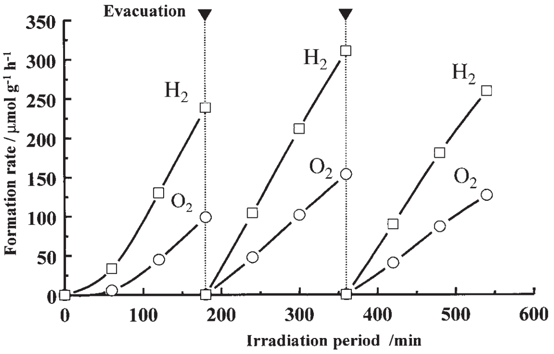

Figure 3. Amount of H_2 and O_2 formed by cyanocobalamin-sensitized Pt/$K_{0.95}Ta_{0.92}Zr_{0.08}O_3$ as a function of reaction time.

a sacrificial agent. The estimated apparent quantum yield of the catalyst for this experiment is 12.2 % with 300-nm light, which is smaller than that reported for La-doped $NaTaO_3$, although it is known that this catalyst exhibits a high quantum yield with UV light.

To identify the effect of the sensitizer, the photovoltaic behavior of Pt/$KTa_{0.92}Zr_{0.08}O_3$ with and without added Cr–TPP was studied as a function of time. Figure 4 shows the decay curve of the photovoltaic potential after irradiation with a 8–10-ns pulse from a 263-nm Nd-YAG laser. When Pt/$KTa_{0.92}Zr_{0.08}O_3$ was irradiated, the photovoltaic potential was observed over 4.0 μs with an estimated half-life of 11.2 μs. It is evident from this figure that the half-life of the photovoltaic potential is increased upon addition of Cr–TPP. This suggests that the lifetime of the photo-excited electron and hole can be increased by coating with Cr–TPP. Therefore the positive effects of porphyrinoids can be explained by the improved efficiency of charge separation. In light of the small bandgap of the organic dye, it is likely that the excited free electron in the $KTaO_3$-based oxide passes to the organic dye, where it is excited again, and then passes to Pt, which is the effective site for H_2 formation, in analogy to photosynthesis. This is because the photovoltaic potential increases upon irradiation with a 263- and 526-nm mixed-laser compared with that of a single 263-nm laser. As previously discussed, TEM observation suggests that the $KTaO_3$ oxide semiconductor is encapsulated by the organic dye, therefore the electron in $KTaO_3$ can easily transfer to the organic dye, resulting in the efficient separation of hole and electron.

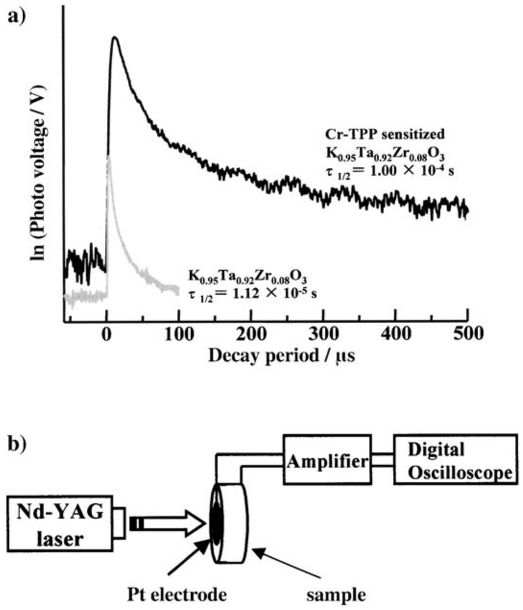

Figure 4. Decay curve of the photovoltaic potential of $KTaO_3$ with and without Cr–TPP sensitization after irradiation for 8–10 ns with a 263-nm laser.

This study has demonstrated that the photocatalytic splitting of water by $KTaO_3$ can be greatly improved by addition of an organic dye as sensitizer and that cyanocobalamin is the most effective dye in this respect.

Experimental Section

The $KTaO_3$ catalyst was prepared by calcination of a mixture of Ta_2O_5, K_2CO_3, and $ZrO(NO_3)_2\cdot 6H_2O$ at 1173 K in air for 10 h. Commercially available organic dye, mainly porphyrin, was used in this study after exchanging the metal center. The various metal porphyrins were prepared by refluxing with the appropriate metal chloride in pyridine. Loading of the dye sensitizer onto the obtained $KTaO_3$ was performed by an impregnation method with pyridine as solvent. Pt was also loaded by an impregnation method with an aqueous solution of $[Pt(NH_3)_4(NO_3)_2]$. The photodecomposition of water was performed in a conventional closed circulating system with a dead volume of about 500 mL. The catalyst (100 mg) was suspended in 30 mL of pure water pre-saturated with Ar. KOH was used to adjust the pH to pH 11. The quartz reaction cell was irradiated by an external light source (500-W Xenon lamp, Ushio). During the photodecomposition the water and catalyst were mixed with a magnetic stirring bar. Argon at a pressure of 10.67 kPa was used as the circulating carrier gas. The H_2 and O_2 formed were measured with a TCD gas chromatograph (Shimadzu GC-8APT) connected to the circulating line with a sampling valve.

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