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Dye Modification Effects on TaON for Photocatalytic Hydrogen Production from Water

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Abstract: Modification effects of porphyrin dyes on the photocatalytic activity of tantalum (oxy)nitride (TaON) were investigated. The nitrogen content in tantalum (oxy)nitride was increased by increasing the heat treatment period. The optimized nitridation conditions were found to be calcination at 800 °C for 14 h under a NH₃ gas flow (25 mL min⁻¹). Among the porphyrin dyes examined, pentamethylene bis[4-(10,15,20-triphenylporphine-5-yl) benzoate]-dizinc (II) (Zn-TPPD) showed the most positive effect on the photocatalytic activity of TaON for H₂ production from Na₂S aqueous solution. From the results of the photocatalytic reaction using various combinations of catalyst components, it was found that the modification dye and PtO_x co-catalysts were necessary to achieving photocatalytic H₂ formation. In the PtO_x/Zn-TPPD/TaON photocatalyst, the expected charge transfer mechanism was a two-step excitation of both TaON and Zn-TPPD, and the oxidation and reduction sites were TaON and PtO_x co-catalyst, respectively. These results indicate that dye modification has the potential to improve the photocatalytic activity of various (oxy)nitride photocatalysts.

Keywords: (oxy)nitride; porphyrin; photocatalyst; hydrogen

1. Introduction

The production of alternative and renewable energy sources is a significant challenge for sustaining the development of human society. Photocatalytic water splitting for converting solar energy to hydrogen energy is one of the ideal solutions for our energy problems. To date, various metal oxide semiconductors, especially Ta-based oxides, have been reported as highly active photocatalysts for water splitting [1–8]. However, these compounds have wide band gaps, which is a disadvantage for solar energy harvesting. Domen *et al.* have reported that oxynitride compounds have the potential to be efficient water splitting photocatalysts [9,10]. Oxynitride compounds have suitable band gaps for visible light absorption and the energy levels of the conduction and valence bands are more negative than the H₂ evolution potential and more positive than the O₂ evolution potential, respectively. Tantalum oxynitride (TaON) is a good candidate for a water splitting photocatalyst due to its stability, suitable conduction and valence band energies [11,12]. The photocatalytic activity of TaON for H₂ and O₂ formation from aqueous solution has been investigated using sacrificial reagents, which are electron donors (e.g., methanol) or acceptors (e.g., silver nitrate) under visible light illumination [13–15]. Compared to the activity for O₂ formation, the activity of TaON for H₂ formation is an order of magnitude lower [13–15]. Thus, improvement of H₂ formation activity is essential for applying TaON as a water splitting photocatalyst.

In our previous studies, we focused on the modification effect of organic dyes (porphyrins, phthalocyanines, and carotenoids) on the photocatalytic activity of inorganic compounds such as KTaO₃ [16–20] or SnS [21]. Specifically, the water splitting activity of the KTaO₃ photocatalyst was much improved by modification with chromium (III) tetraphenyl porphyrin chloride (Cr-TPPCL). The Cr-TPPCL physically adsorbed on the KTaO₃ surface and worked as a photo-excited electron acceptor for KTaO₃, thus prolonging the charge separation state of KTaO₃. Furthermore, from the results of the wavelength dependency of the photocatalytic activity, the water splitting reaction on the dye-modified KTaO₃ proceeded via a two-step excitation of both KTaO₃ and dye similar to photosynthesis in green plants. The reduction potential of the photo-excited electron was increased from the conduction band level of KTaO₃ to the LUMO level of the porphyrin dyes. Thus, H₂ formation activity was improved, showing that dye modification has the potential to improve the reduction ability of inorganic photocatalysts. In this study, we applied this dye modification method to improve the H₂ formation activity of tantalum (oxy)nitride. The tantalum (oxy)nitrides were modified with five different types of porphyrin dyes, and the influence of adsorption states (physical adsorption and covalent attachment) and the photocatalytic activities of each were investigated.

2. Results and Discussion

Crystal structures of (oxy)nitride samples were determined by X-ray diffraction (XRD). Figure 1 shows the XRD patterns for Ta₂O₅ and (oxy)nitride samples prepared at 800 °C for various heat treatment times under NH₃ gas flow. In this paper, the prepared (oxy)nitride samples are named according to the heat treatment time, e.g., ON-12 is the (oxy)nitride sample treated for 12 h. The XRD patterns showed that the crystal structures of the (oxy)nitride samples were influenced by the treatment time. The ON-12 consisted of TaON (JCPDS No. 71-0178) and a small amount of orthorhombic Ta₂O₅

(JCPDS No. 25-0922). From energy dispersive X-ray spectrometry (EDX), it was confirmed that ON-12 contains 2.9% of Ta_2O_5 . The XRD pattern of ON-14 was assigned to that of TaON. In these heat treatment processes, TaON was formed according to the following equation [22]:

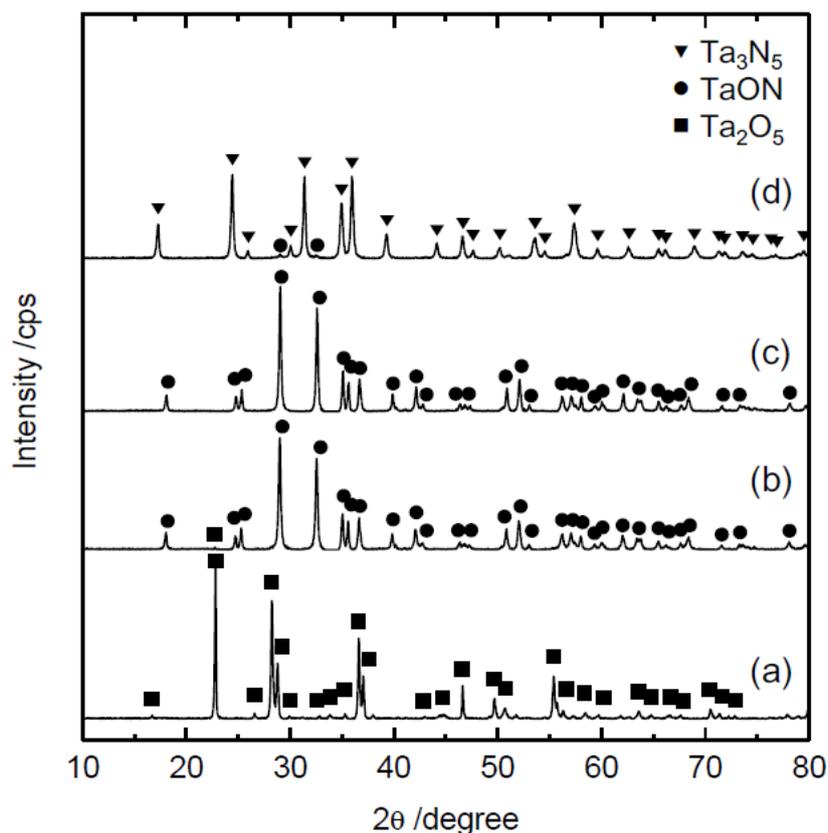


As shown in Figure 1(d), excessive treatment time led to the formation of Ta_3N_5 (JCPDS No. 79-1533), which is the nitrated phase of TaON formed as in the following equation:



Because these nitridation processes are endothermic [23], the content of nitrogen increased with an increasing heat treatment period under the preparation conditions in this study. In the case of ON-24, the content of TaON was calculated as 6.6%.

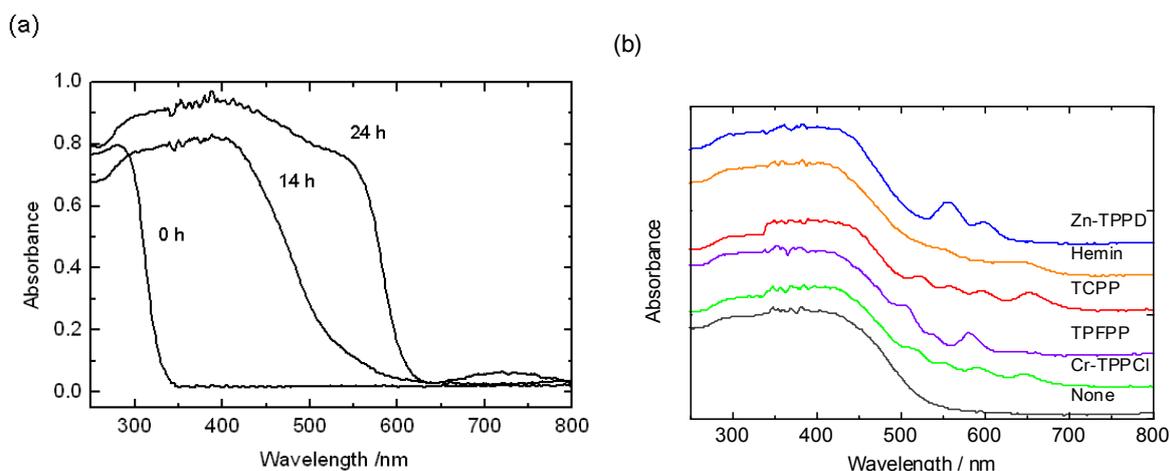
Figure 1. XRD patterns of (a) Ta_2O_5 and tantalum (oxy)nitride samples: (b) ON-12; (c) ON-14, and (d) ON-24.



The colors of ON-12, ON-14, and ON-24 are yellow, dark yellow and orange, respectively. Figure 2(a) shows UV-vis diffuse reflectance spectra of Ta_2O_5 and (oxy)nitride samples. The absorption spectrum of ON-12 is not shown in Figure 2(a) because it is almost the same as that of ON-14. Compared with the spectrum of Ta_2O_5 , both (oxy)nitride samples showed strong visible light absorptions in the wavelength range from 350 to 600 nm. The absorption edges of ON-14 and ON-24 were approximately 550 and 615 nm, respectively. The band gaps of TaON and Ta_3N_5 were reported as 2.4 and 2.1 eV from electrochemical analysis and ultraviolet photoelectron spectroscopy (UPS) [24].

Strong visible light absorption of ON-24 was attributed to the photoabsorption of Ta_3N_5 . Figure 2(b) shows UV-vis diffuse reflectance spectra of ON-14 modified with various porphyrin dyes. The porphyrin dyes used in this study are as follows: chromium tetrphenyl porphyrin chloride (Cr-TPPCL), hemin, pentamethylene bis[4-(10,15,20-triphenylporphine-5-yl) benzoate]-dizinc (II) (Zn-TPPD), tetrakis(4-carboxyphenyl)porphyrin (TCPP), and 5,10,15,20-tetrakis(pentafluorophenyl)-21H, 23H-porphyrin (TPFPP). Compared with the absorption spectrum of ON-14, dye-modified ON-14 showed photoabsorption peaks in the wavelength range from 500–700 nm. These absorption peaks are attributed to the Q-band absorption of porphyrin dyes adsorbed on the surface of ON-14. Therefore, it is expected that visible light from 500 to 700 nm could be used for the photocatalytic reaction.

Figure 2. UV-vis diffuse reflectance spectra of (a) Ta_2O_5 and tantalum (oxy)nitride samples and (b) ON-14 modified with various porphyrin dyes.



X-ray photoelectron spectroscopy (XPS) was used to investigate the oxidation state of the (oxy)nitride samples and confirm the nitrogen doping. Figure 3 shows the O 1s, N 1s, and Ta 4d orbitals of XPS spectra of Ta_2O_5 , ON-14, and ON-24. The binding energy was normalized by adjusting the C 1s peak to 284.6 eV. The peak area of the O 1s spectra decreased with increasing heat treatment period, while that of the N 1s spectra increased. The nitrogen content of the (oxy)nitride samples was expected to increase based on the results of the XRD analysis, and the XPS spectra of O 1s and N 1s clearly indicated that N atoms replaced O atoms by the heat treatment under NH_3 gas flow. Compared with the Ta 4d peaks of Ta_2O_5 , the Ta 4d peaks of the (oxy)nitride samples shifted to lower binding energy after heat treatment. Some Ta atoms were reduced during nitridation, and the reduced Ta might have produced defects that functioned as trap sites for photogenerated electrons and holes. Therefore, the heat treatment time for preparation of (oxy)nitride samples was optimized at 14 h.

Figure 4 shows Pt 4f XPS spectra of the Pt-loaded Zn-TPPD/ON-14 sample. The Pt 4f_{5/2} and 4f_{7/2} peaks of the loaded Pt are fitted to four Gaussian peaks. The XPS peaks at 74.4 eV (4f_{7/2}) and 78.3 eV (4f_{5/2}) were almost the same as those for PtO₂. The other peaks at 73.4 eV and 76.4 eV appeared between the Pt 4f peaks of PtO₂ and Pt foil. These peaks were attributed to PtO, which has been reported in several papers [25–27]. Therefore, it was found that the oxidation states for the Pt particles were Pt²⁺ (PtO) and Pt⁴⁺ (PtO₂) on the Zn-TPPD/ON-14. It has been reported that oxidized Pt effectively improved the photocatalytic activity when used as a co-catalyst [28]. Therefore, PtO and

PtO₂ (PtO_x) as co-catalysts loaded on the dye-modified (oxy)nitride were expected to serve as reaction sites and decrease the overpotential of hydrogen formation.

Figure 3. XPS spectra of O 1s, N 1s, and Ta 4d in (a) Ta₂O₅; (b) ON-14 and (c) ON-24.

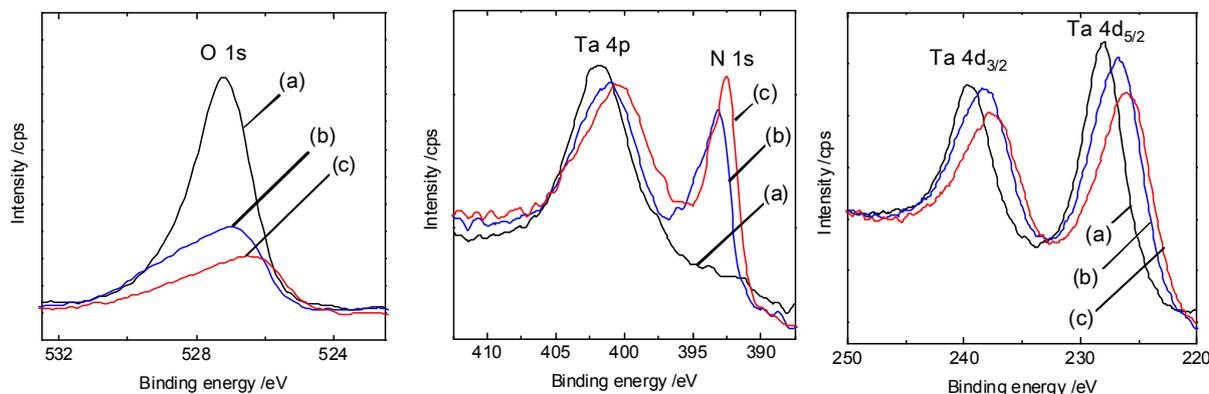
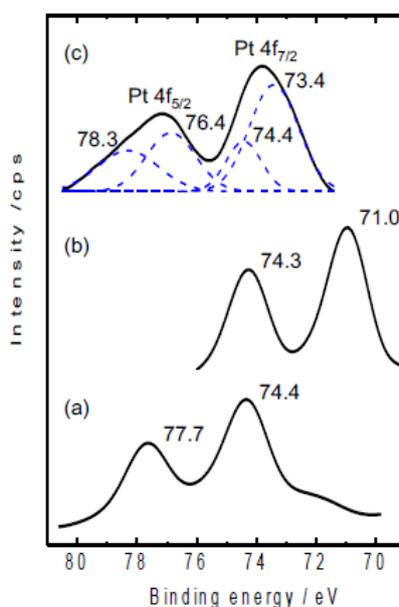


Figure 4. XPS spectra of Pt4f in (a) PtO₂; (b) a Pt foil, and (c) Pt loaded on Zn-TPPD/ON-14.



The photocatalytic activities of dye-modified (oxy)nitrides were tested in sodium sulfide (Na₂S) aqueous solution. Since some porphyrin dyes dissolved in aqueous alcohol (ethanol or methanol) solutions, Na₂S was employed as a sacrificial reagent for hydrogen formation. The hydrogen formation process under this experimental condition is as follows:

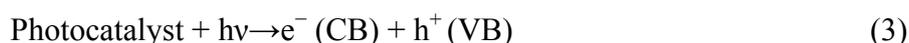


Table 1 shows the effect of dye modification on the catalytic activity of Pt-loaded (oxy)nitride (ON-14) under visible light irradiation. The modification dyes were selected on the basis of the results from

dye-modified KTaO_3 photocatalysts for water splitting [17]. Except for hemin, the porphyrin dyes showed a positive effect on the photocatalytic H_2 formation. In these dyes, TCPP and hemin formed covalent attachments with the ON-14 surface with their carboxyl groups, and the other dyes attached by physical adsorption. The porphyrin dyes attached with physical adsorption showed more positive effects on the photocatalytic activity of ON-14. These dyes were adsorbed onto the ON-14 surface via the porphyrin ring, which may function as the electron acceptor for ON-14. The distance between the porphyrin ring and the TaON surface was shorter than that for TCPP or hemin. This is an advantage for electron transfer between porphyrin dyes and TaON, and thus, the photocatalytic activity of ON-14 was much improved by modification with physically adsorbed dyes. Among the porphyrin dyes examined, the H_2 formation rate for $\text{PtO}_x/\text{Zn-TPPD}/\text{ON-14}$ was the highest ($95.6 \mu\text{mol g}^{-1}\text{h}^{-1}$). In the case of $\text{PtO}_x/\text{Zn-TPPD}/\text{ON-14}$, the turnover number (TON) calculated from the amount of formed H_2 and porphyrin dye used was 173.6. From the UV-vis absorption spectral measurement, it was confirmed that Zn-TPPD remained after the photocatalytic reaction under visible light irradiation for 6 h. Thus, the porphyrin dyes improved the photocatalytic activity without decomposition.

Table 1. Dye modification effect on H_2 formation from Na_2S aqueous solution over PtO_x (0.2 wt%)/Dye (0.5 wt%)/(oxy)nitride (ON-14) photocatalyst.

Dye	H_2 formation rate $/\mu\text{mol g}^{-1}\text{h}^{-1}$	TON (formed H_2/dye)
Zn-TPPD	95.6	173.6
Cr-TPPCl	75.1	59.9
TPFPP	59.3	69.4
TCPP	30.6	29.0
None	7.7	-
Hemin	1.2	1.0

Light source: 300 W Xe lamp with 420 nm long pass filter; reaction time: 6 h; amount of catalyst: 0.1 g; 0.24 M Na_2S aqueous solution.

In order to reveal the role of the modification dye in $\text{PtO}_x/\text{Zn-TPPD}/\text{ON-14}$, the photocatalytic activities of the catalyst components combined in various ways for H_2 or O_2 formation reactions were investigated. Silver nitrate (AgNO_3) was used as a sacrificial reagent for the O_2 formation reaction. Figure 5 shows the photocatalytic activities of the catalyst components for H_2 and O_2 formation from sacrificial reagent aqueous solution. For the H_2 formation from Na_2S aqueous solution, $\text{PtO}_x/\text{Zn-TPPD}/\text{ON-14}$ showed the highest photocatalytic activity. Despite the existence of all components, the H_2 formation rate for $\text{Zn-TPPD}/\text{PtO}_x/\text{ON-14}$, which was prepared by coating Zn-TPPD on $\text{PtO}_x/\text{ON-14}$, was lower than that for $\text{PtO}_x/\text{Zn-TPPD}/\text{ON-14}$. This strongly suggests that PtO_x works as a co-catalyst for H_2 formation at the surface of Zn-TPPD coated ON-14. $\text{PtO}_x/\text{ON-14}$ and $\text{Zn-TPPD}/\text{ON-14}$ showed low photocatalytic activity, and no H_2 formation was observed over ON-14 and $\text{PtO}_x/\text{Zn-TPPD}$. Thus, the existence of all components (ON-14, dye, and co-catalyst) in conjunction with the preparation procedure was important to improve the photocatalytic activity of dye-modified (oxy)nitride photocatalysts for H_2 formation. On the other hand, in the case of the O_2 formation reaction from AgNO_3 aqueous solution, almost the same formation rates were observed with the

exception of that for PtO_x/Zn-TPPD. These results suggest that the reduction and oxidation reaction sites of the PtO_x/Zn-TPPD/ON-14 photocatalyst are the Pt co-catalyst and ON-14 surface, respectively, unlike the case for general dye-sensitized photocatalysts [29,30]. Although the PtO_x/Zn-TPPD/ON-14 photocatalyst could form H₂ and O₂ from sacrificial reagent solutions, complete photocatalytic water splitting did not proceed on this photocatalyst. The oxygen or nitrogen defects in (oxy)nitride may trap the excited charge and complete photocatalytic water splitting reaction on the PtO_x/Zn-TPPD/ON-14 photocatalyst is prevented.

Figure 5. Photocatalytic activities of the combination of PtO_x, Zn-TPPD, and TaON (ON-14) for H₂ and O₂ formation reaction from sacrificial reagent aqueous solution.

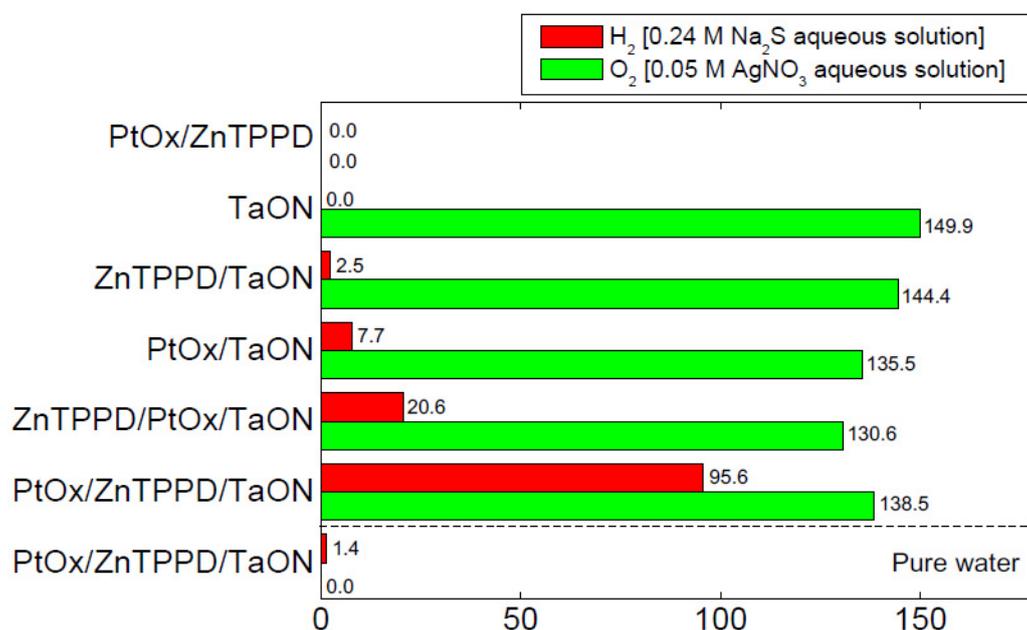
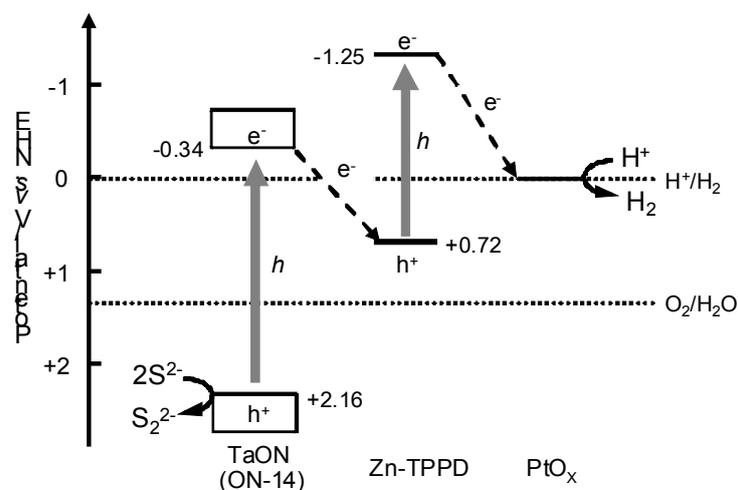


Figure 6 shows the expected charge transfer mechanism for PtO_x/Zn-TPPD/ON-14. The conduction and valence band energies for TaON were adapted from reference [24]. In the case of Zn-TPPD, the HOMO and LUMO levels were determined from the redox potential and the band gap was estimated from the photoabsorption and photoluminescence spectra. The LUMO level for Zn-TPPD was estimated to be -1.25 V, which is more negative than the conduction band level for TaON. Different from the charge transfer mechanism in the dye sensitization system, photo-excited electrons in Zn-TPPD transfer to the PtO_x co-catalysts, which might be the reaction site for H₂ formation. The oxidized Zn-TPPD is reduced by photo-excited electrons in ON-14, and the photo-generated holes in ON-14 oxidize the hole scavenger (S²⁻). Zn-TPPD plays a role in absorbing visible light and improving the reduction ability of TaON. Although complete photocatalytic water splitting was not achieved on the dye-modified TaON photocatalyst, this study reveals that modification with porphyrin dye is an effective method for improving the photocatalytic activity of the hydrogen formation reaction on TaON.

Figure 6. Expected charge transfer mechanism in PtO_x/Zn-TPPD/ON-14 photocatalyst.

3. Experimental Section

For the preparation of the tantalum (oxy)nitride, Ta₂O₅ powder (5.0 g, Kojundo Chemical Laboratory Co., Ltd., Kariya, Japan) was used as the starting material and placed onto an alumina combustion boat (width: 15 mm; height: 13 mm; length: 90 mm; Nikkato Corp., Sakai, Japan) and heated in an alumina-tube furnace (ϕ : 30 mm) at 800 °C under a NH₃ gas flow (25 mL min⁻¹). Except for Cr-TPPCl, all porphyrin dyes, Zn-TPPD [Tokyo Chemical Industry Co., Ltd. (TCI), Tokyo, Japan], TPFPP (TCI), TCPP (TCI), and hemin (TCI) were commercially available and used without further purification. Cr(III)-TPPCl was prepared by a refluxing method published by Adler and coworkers [31]. H₂TPP (1.0 g, >98.0%, chlorine free, TCI) was dissolved in 300 mL of *N,N*-dimethylformamide (DMF). Several minutes after the reflux started, CrCl₂ (1.0 g, 99.99%, Sigma-Aldrich Co., Ltd., St. Luis, MO, USA) was added to the DMF solution. The reaction mixture was cooled to room temperature, and then poured into a beaker containing 300 mL of chilled ice water. The obtained products were collected by filtration, and dried in a vacuum oven for 1 h at 100 °C. The yield of crude Cr-TPPCl was 64.1%. Purification of Cr-TPPCl was performed by column chromatography. Crude Cr-TPPCl (0.2 g) was dissolved in 50 mL of dichloromethane (CH₂Cl₂), and then applied to a silica gel column (Merck, silica gel 60, 40–63 μ m) and eluted with CH₂Cl₂. Unreacted H₂TPP was promptly eluted as a red band with the solvent front, and Cr-TPPCl was eluted as a green band. After the Cr-TPPCl was eluted from the column, the CH₂Cl₂ was removed with a rotary evaporator. The complex was dried for 3 h in a vacuum oven at 100 °C. The yield of purified Cr-TPPCl was 41.2%. The dye modification of tantalum (oxy)nitrides was performed by an evaporation to dryness method with pyridine as the solvent. The (oxy)nitride powder was suspended in dye-dissolved pyridine (0.5 mM) and the solvent was evaporated to dryness by stirring with a glass rod at 130 °C. The amount of modification dye was calibrated as 0.5 wt% of the amount of tantalum (oxy)nitride sample in this study. The platinum co-catalyst was loaded on the dye-modified tantalum (oxy)nitride by an evaporation to dryness method with Pt(NH₃)₄(NO₃)₂ (Sigma-Aldrich Co., St. Luis, MO, USA) aqueous solution, followed by drying on a hot plate at 100 °C. The loading amount of co-catalyst on the dye-modified tantalum (oxy)nitride photocatalysts was 0.1 wt%.

The photocatalytic reaction was performed with a conventional closed circulating system with a dead volume of ca. 500 mL. The catalyst (100 mg) was suspended in 30 mL of reaction solution, which was pre-saturated with Ar. The concentrations of Na₂S and AgNO₃ aqueous solution were 0.24 M and 0.05 M, respectively. A quartz reaction cell was irradiated by an external light source consisting of a 500 W Xe lamp (Ushio Inc., SX-UI500XQ, Tokyo, Japan). During the photocatalytic reaction, the suspension was mixed using a magnetic stirring bar. Ar gas (10.67 kPa) was used as the circulating carrier gas. Before the reaction started, the absence of gas leakage was confirmed for 1 h by performing a reaction in the absence of light. The amount of H₂ or O₂ formed was measured by a gas chromatograph with a thermal conductivity detector (Shimadzu Corp., GC-8A, Kyoto, Japan), which was connected to a conventional volumetric circulating line with a vacuum pump.

The crystal structure was analyzed by X-ray powder diffraction (RINT-2500, Rigaku, Tokyo, Japan), in conjunction with Cu K α radiation, operated at 40 kV, 80 mA, and a scanning rate of 4°/min within the range of 2 θ from 10 to 80°. UV-vis absorption spectra were obtained by a reflection method using a spectrophotometer (U-3310, HITACHI, Tokyo, Japan) with an integrating sphere attachment and a KBr pellet was used as the reference. X-ray photoelectron spectroscopy (XPS) was performed with an X-ray photoelectron spectrometer (Shimadzu Co. Ltd., ESCA-3400, Kyoto, Japan) using a Mg K α irradiation source. Each spectrum was normalized by adjusting the C 1s peak to 284.6 eV. The compositions of the tantalum (oxy)nitrides were determined using scanning electron microscopy-EDX (SEM-EDX, VE-7800, Keyence Corp., Osaka, Japan). The catalyst sample was mounted on a circular metallic sample holder. The EDX analysis was performed at an acceleration voltage of 20 kV without a coating conductive layer.

4. Conclusions

Modification effects of porphyrin dyes on the photocatalytic activity of tantalum (oxy)nitride (TaON) were investigated. For the preparation of TaON, the heat treatment conditions were optimized at 800 °C for 14 h under NH₃ gas flow (25 mL min⁻¹). Among the porphyrin dyes examined, pentamethylene bis[4-(10, 15, 20-triphenylporphine-5-yl) benzoate]-dizinc (II) (Zn-TPPD) showed the most positive effect on the photocatalytic H₂ formation from the Na₂S aqueous solution. The photocatalytic activity tests on the photocatalyst components indicated that the H₂ formation site was the Pt co-catalyst and the oxidation reaction site was the tantalum (oxy)nitride in the PtO_x/Zn-TPPD/ON-14 photocatalyst. This study revealed that the role of the modification dye was to absorb visible light and improve the reduction ability of TaON.

Acknowledgments

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Conflict of Interest

The authors declare no conflict of interest.

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