Conduction and Valence Band Positions of Ta_2O_5, TaON, and Ta_3N_5 by UPS and Electrochemical Methods

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The conduction and valence band edges for electronic band gaps and Fermi levels are determined for Ta_2O_5, TaON, and Ta_3N_5 by ultraviolet photoelectron spectroscopy (UPS) and electrochemical analyses. Reasonable agreement between the results of the two methods is obtained at the pH at which the ζ potentials of the particles are zero. The tops of the valence bands are found to be shifted to higher potential energies on the order Ta_2O_5 < TaON < Ta_3N_5, whereas the bottoms of the conduction bands are very similar in the range −0.3 to −0.5 V (vs NHE at pH = 0). From the results, it is concluded that TaON and Ta_3N_5 are promixing catalysts for the reduction and oxidation of water using visible light in the ranges λ < 520 nm and λ < 600 nm, respectively. It is also demonstrated that the proposed UPS technique is a reliable alternative to electrochemical analyses for determining the absolute band gap positions for materials in aqueous solutions that would otherwise be difficult to measure using electrochemical methods.

1. Introduction

For most photoelectronic applications of semiconductors and insulators, the knowledge of absolute band gap positions is essential. The present authors have been investigating the utilization of various oxides and non-oxide materials as photocatalysts for overall water splitting in an effort to achieve efficient photochemical energy conversion.[1−3] The thermodynamic requirements for solid-state photocatalysts suitable for overall water splitting are as follows.

The bottom of the conduction band E_{CB} should be more negative than the H^+/H_2 redox potential, that is, 0 V vs NHE at pH = 0 (or the electron potential should be more positive than −4.44 eV vs the vacuum level).

The top of the valence band E_{VB} should be more positive than the O_2/OH^- redox potential, that is, +1.23 V vs NHE at pH = 0 (or more negative than −5.6 eV vs the vacuum level).

At present, the authors are concentrating on developing promising materials for overall water splitting under visible light irradiation (400 nm < λ < 800 nm). A number of oxynitrides of early transition metals such as Ti[4] and Ta[5,6] have been found to be potential candidates for this application. However, the band gap positions of these materials are unknown, and in most cases the fabrication of suitable electrodes has been unsuccessful due to difficulties in processing the powder samples. Therefore, the authors have begun to use photoelectron spectroscopy, and ultraviolet photoelectron spectroscopy (UPS) in particular, to determine the band gap positions of these materials. This method is a useful technique for this situation because the correlation between the photoelectrode potential and the absolute potential of electrons has already been established.[7] The sole difficulty in performing UPS measurements for such wide band gap and low-conductivity materials is undesirable charging of the samples during measurement.

In this study, Ta_2O_5, TaON, and Ta_3N_5 samples prepared by several methods are analyzed by electrochemical methods and UPS to determine the band gap positions and to confirm the validity of UPS analysis for this purpose.

2. Experimental Section

2.1. Sample Preparation. Two different series of samples were prepared. One series was prepared from Ta foil for analysis by electrochemical methods and UPS. The Ta foil (10 × 10 × 0.2 mm^3, 99%, Nilaco Co.) was oxidized at 823 K in air for 30 min to give a Ta_2O_5/Ta sample, and a Ta_3N_5/Ta sample was obtained by exposing a Ta_2O_5/Ta foil sample to NH_3 at 1123 K and a flow rate of 20 mL/min for 4 h. The authors also attempted to prepare TaON/Ta; however, the surface layer peeled off easily for all samples and a suitable preparation condition was not found. The second series was prepared from powder samples. TaON and Ta_3N_5 powders were synthesized by the following procedures according to the literature.[8] Bright yellow TaON was obtained by exposing Ta_2O_5 (99%, Rare Metallic Co., Ltd.) to NH_3 (99.999%, Mitsui Chemicals Co. Ltd.) at 1023 K and a flow rate of 20 mL/min for 20 h. Pure wine-red Ta_3N_5 was prepared by a similar method at 1123 K

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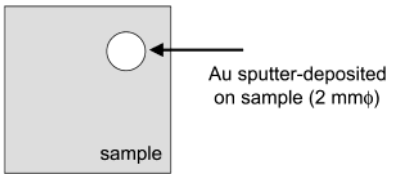

Figure 1. Schematic illustration of sample coated with Au.

and a flow rate of 1000 mL/min for 10−15 h. Initially, powder samples pressed into disks were employed for UPS measurement; however, reliable and reproducible data could not be obtained due mainly to sample charging. Therefore, samples were prepared by electrophoretic deposition on Pt foils.[9,10] TaON or Ta_3N_5 powder (50 mg) was suspended in 50 mL of acetone containing 10 mg of I_2 by ultrasonication. The electrophoretic deposition of TaON or Ta_3N_5 was performed using a thin Pt foil ($25 \times 10 \times 0.1$ mm^3) as an anode. Deposition was carried out for 1 min at 20 V. The prepared sample was then washed thoroughly with acetone prior to UPS measurement.

2.2. Characterization. Samples were characterized by atomic force microscopy (AFM; TMX-2100, TopoMetrix), X-ray diffractometry (XRD; Geigerflex Rad-B system Cu Kα 15 mA, Rigaku), field-emission scanning electron microscopy (FE-SEM; S-4700, Hitachi) and UV−visible diffuse reflectance spectroscopy (UV−vis DR; V-560, JASCO). X-ray photoelectron spectroscopy (XPS) was performed using a VG-ADES 400 instrument (Vacuum Generators Co.) with Mg Kα X-ray source at a residual gas pressure of below 10^{-8} Pa. The binding energy was calibrated against Au 4f $_{7/2}$ (83.9 eV).

2.3. Electrochemical Measurement. A Cu wire was attached to the Ta_2O_5/Ta or Ta_3N_5/Ta foil with silver paste, and all samples were waterproofed, except for the front surface, with epoxy resin to prevent current leakage. A Pyrex electrolytic cell was employed, filled with 20 mL of Ar-purged 0.5 M K_2SO_4. The pH of the solution was adjusted with 0.1 M NaOH and 0.1 M H_2SO_4. A Pt wire and Ag/AgCl electrode were employed as the counter and reference electrodes, respectively. Impedance measurements were recorded using a frequency response analyzer (Hz-3000, Hokuto, Ltd.).

2.4. UPS Measurement. UPS spectra were measured using He I excitation (21.2 eV) and recorded with a constant pass energy of 5 eV in the ultrahigh vacuum (UHV) chamber of the XPS instrument. UPS binding energies were referenced to the Fermi edge of Au, which was sputtered onto the sample in the UPS chamber. Figure 1 shows an illustration of a foil coated with Au. The spot diameters of the deposited Au and UV light were 2 mm. None of the samples were damaged in these measurements. Prior to XPS and UPS measurements, the Ta_2O_5/Ta sample was oxidized at 823 K for 30 min in the UHV chamber in an O_2 (99.999% purity) atmosphere at 5×10^{-3} Pa to remove surface impurities. To maintain the purity of O_2 in the UHV chamber, the chamber was evacuated to 10^{-5} Pa and charged with fresh O_2 every 5 min. The TaON/Pt, Ta_3N_5/Ta, and Ta_3N_5/Pt samples were subjected to low-temperature H_2 treatment to remove surface contamination. The samples were heated for 1 h at 523 K in the UHV chamber in an H_2 (99.999% purity) atmosphere at 5×10^{-3} Pa. Fresh H_2 was introduced every 10 min.

2.5. Measurement of ζ Potential. The ζ potential was measured on a DELSA 440SX (Coulter). The suspension fluid was a 0.01 M aqueous solution of KCl with pH adjusted by the addition of 0.01 M HCl and 0.01 M KOH solutions.

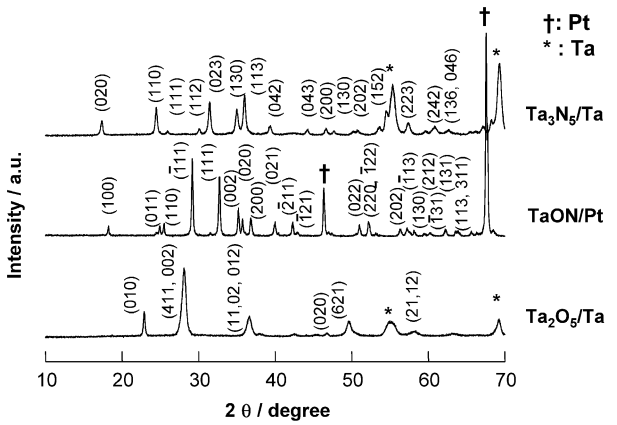

Figure 2. X-ray diffraction patterns of Ta_2O_5/Ta, TaON/Pt, and Ta_3N_5/Ta.

3. Results

3.1. XRD, SEM, AFM, and UV−Vis DRS. XRD patterns of Ta_2O_5/Ta, TaON/Pt and Ta_3N_5/Ta are shown in Figure 2. All diffraction peaks were assigned to Ta_2O_5, TaON, and Ta_3N_5, respectively, in addition to the substrate materials.[11,12] No impurity phases were observed.

Figure 3 shows SEM images of Ta_2O_5/Ta, Ta_3N_5/Ta, and TaON/Pt. The surfaces of Ta_2O_5/Ta (a) and Ta_3N_5/Ta (b) were essentially flat, with several cracks. TaON particles electrophoretically deposited on Pt were estimated to be 0.5−1.0 μm in diameter, and the Pt substrate surface could not be observed, as shown in Figure 3c,d.

Figure 4 shows the AFM image of the TaON/Pt sample. The dark (lower) part of the image is a bare Pt area where TaON deposition was prevented. From the difference in height between the bare and coated Pt areas, the thickness of the TaON film was estimated to be about 2 μm.

Figure 5 shows the UV−vis DR spectra for powder samples of Ta_2O_5, TaON, and Ta_3N_5. TaON/Pt was prepared from TaON powder by electrophoretic deposition. The Ta_3N_5/Pt sample was also prepared by electrophoretic deposition with Ta_3N_5 powder. The spectra of TaON/Pt and Ta_3N_5/Pt should be the same with the powder samples. The values of E_{BG} were, therefore, determined by UV−vis DR spectra for powder samples in this paper. In the UV−vis spectra, the absorption band edges of TaON and Ta_3N_5 occur at 520 and 600 nm, respectively, and are shifted by about 200 and 280 nm from that of Ta_2O_5. The band gap energies (E_{BG}) of Ta_2O_5, TaON and Ta_3N_5 were estimated to be 3.9, 2.4, and 2.1 eV, respectively.

3.2. XPS Analysis. XPS was used to examine the surface composition of Ta, N, and O and the oxidation state of Ta in the samples. Figure 6 shows the O1s, N1s, and Ta4f spectra of Ta_2O_5/Ta, TaON/Pt and Ta_3N_5/Ta, respectively. Peak positions are summarized in Table 1. Sample charging was often observed for the oxide powders, but was not observed for the thin-film samples including TaON/Pt. The peak positions of the O1s spectra were very similar in all samples. The observed O1s spectrum of Ta_3N_5/Ta most likely contains information from the area out side the sample. The spot size of the irradiated X-ray is much larger than the He I used for the UPS measurement, which is 2 mm in diameter. Judging from actual intensity, the contribution of the surface oxygen on Ta_3N_5/Ta should be negligibly small for UPS measurement.

No Ta^0 or Pt^0 metal peak was observed in any of the samples, indicating that the substrate was completely obscured. In Ta_2O_5/Ta, Ta $4f_{7/2}$, and Ta $4f_{5/2}$ peaks appeared at 26.6 and 28.5 eV, respectively. These energy values correspond to Ta^{5+} in Ta_2O_5

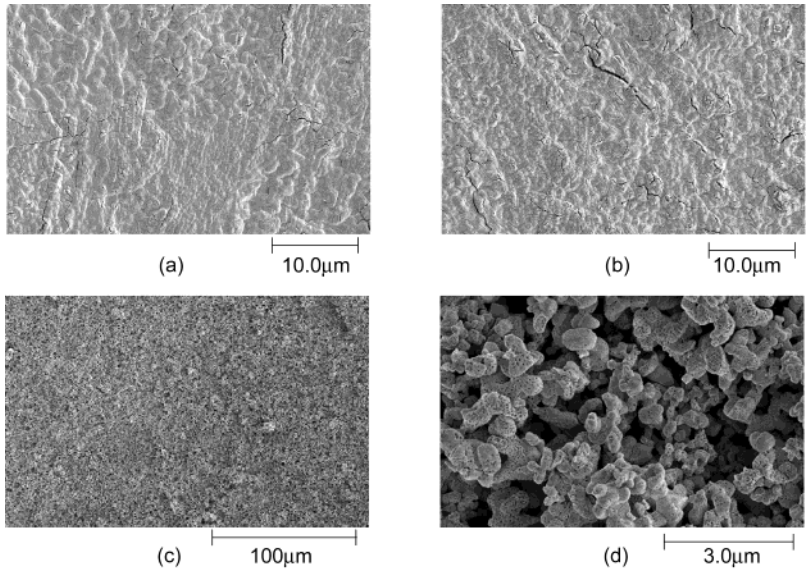

Figure 3. SEM image of (a)Ta_2O_5/Ta, (b)Ta_3N_5/Ta, and (c,d)TaON/Pt.

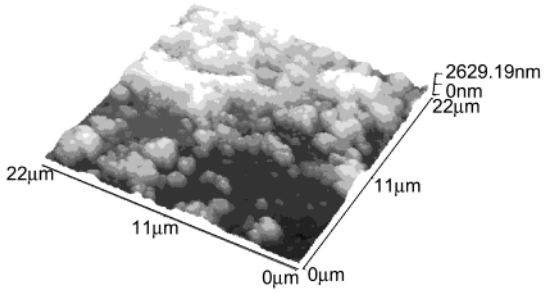

Figure 4. AFM image of TaON/Pt.

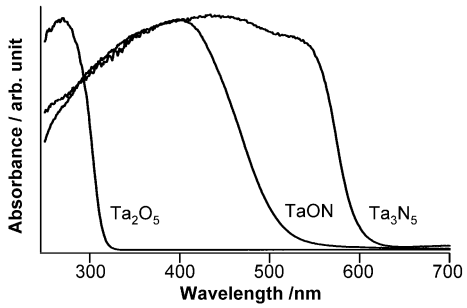

Figure 5. U−-vis diffuse reflectance spectra of Ta_2O_5, TaON, and Ta_3N_5.

TABLE 1: Binding Energies of O 1s, N 1s, Ta $4f_{5/2}$, and Ta $4f_{7/2}$ Peaks for Ta_2O_5/Ta, TaON/Pt, and Ta_3N_5/Ta

electrodes	O 1S/eV	N 1S/eV	Ta $4f_{5/2}$/eV	Ta $4f_{7/2}$/eV
Ta metal	N/A	N/A	23.7	21.8
Ta_2O_5/Ta	530.9	N/A	28.5	26.6
TaON/Pt	530.8	397.1	27.7	25.8
Ta_3N_5/Ta	530.7	396.5	26.7	24.8

as reported in the literature.[13] Ta4f peaks for TaON/Pt and Ta_3N_5/Ta are shifted to lower binding energies by ca. 0.8 and 1.8 eV compared to those of Ta_2O_5. Considering the difference in electronegativity between O and N, it is considered that the electron density around Ta atom increases with the N/O ratio. In other words, the covalency between Ta and N is greater than between Ta and O. This kind of difference could affect the band gap positions of these materials.

3.3. Electrochemical Measurements. To estimate flat band potentials (E_{FB}), plots of (differential capacitance)$^{-2}$ against electrode potential (Mott−Schottky plots) under different pH conditions for both electrodes were constructed, as shown in Figure 7. It was found that the flat band potential of Ta_2O_5 depends almost linearly on the pH of the electrolyte solution with a slope of ca. −60 mV/ΔpH as seen in Figure 7a. It is known that oxide semiconductors in general react with H^+ or OH^- ions in solution, and the band edges at the interface consequently shift with the pH of the solution by 60 mV per pH unit change in the solution. Interestingly, it was also found that the E_{FB} of Ta_3N_5 varies linearly with pH, as seen in Figure 7b. Huygens reported that the E_{FB} of GaN is also a linear function of pH.[14] The E_{FB} of Ta_2O_5 is approximately −1.3 V vs Ag/AgCl (−1.1 V vs NHE) at pH = 13 and −0.5 V vs Ag/AgCl at pH = 0 (−0.3 V vs NHE), and the E_{FB} of Ta_3N_5 is approximately −1.0 V vs Ag/AgCl (−0.8 V vs NHE) at pH = 13 and −0.3 V vs Ag/AgCl at pH = 0 (0.0 V vs NHE). Impedance measurements could not be completed for the TaON/Pt electrode because the electrolyte penetrated down to the Pt substrate.

3.4. UPS Measurement. As an example, UPS spectra of TaON/Pt measured at various sample biases (0, −10, and −15 V) are shown in Figure 8. The cutoff of the UPS spectrum (or low kinetic energy region) with the sample bias of 0 V cannot be observed clearly. The cutoff position ($E_K = 0$ eV) needs to be identified to estimate the vacuum level, and sample biases higher than the work function allow this to be achieved. At −10 and −15 V, clear cutoffs could be observed in the UPS spectra, as shown in Figure 8. The following equation should then hold:

$$E_B + E_K + \phi_{analyzer} = 21.2 \text{ eV} \quad (1)$$

where E_B, E_K and $\phi_{analyzer}$ are the binding energy measured from the Fermi level, the kinetic energy of the electron, and the work function of the analyzer. Therefore, $\phi_{analyzer}$ was found to be smaller than 10 eV, and an applied potential of 10 eV was sufficient to capture the entire spectrum.

Features in the valence band and the entire spectrum remained unchanged with respect to the different biases, although the background attributed to secondary electron emission was reduced. It should be noted that none of the samples charged up during UPS measurement as in the case for XPS measurement. Figure 9 shows the UPS spectra of TaON/Pt and Au on TaON/Pt. The Fermi level of Au on TaON/Pt was estimated to

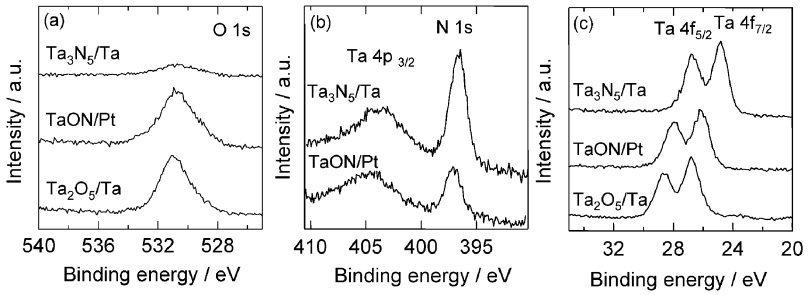

Figure 6. X-ray photoelectron spectra of Ta_2O_5/Ta, TaON/Pt, and Ta_3N_5/Ta: (a) O1s, (b) N1s, and (c) Ta4f regions.

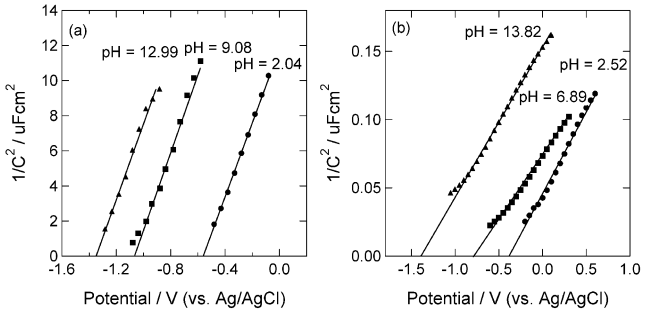

Figure 7. Mott−Schottky plots of (a) Ta_2O_5 and (b) Ta_3N_5 under various pH conditions.

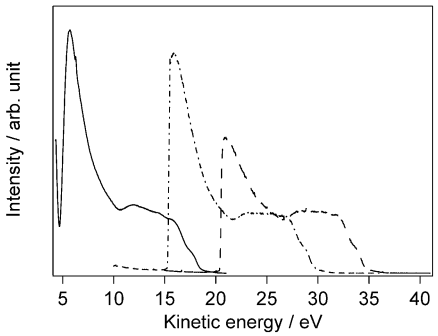

Figure 8. UPS spectra of TaON/Pt measured at various sample biases. Solid line: 5 V. Dash−dotted line: 10 V. Dashed line: 15 V.

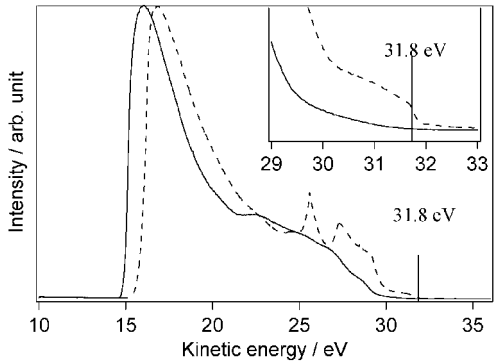

Figure 9. UPS spectra of TaON/Pt (solid line) and Au on TaON/Pt (dashed line).

be at $E_K = 31.8$ eV in the spectrum. The Fermi level of TaON/Pt is at the same position as that of Au deposited on TaON/Pt, which allows the Fermi level to be determined experimentally.

The relationship between several energy levels (E_{VB}, E_F, and E_{vac}) and the UPS spectrum of TaON/Pt and Au is shown in Figure 10. The figure shows the scale of binding energy with the Fermi level of Au set at 0 V. The vacuum level (E_{vac}) should be located 21.2 eV above the cutoff energy of the spectrum. The work functions of TaON and Au based on this definition are estimated to be 4.4 and 5.1 eV, respectively. The work

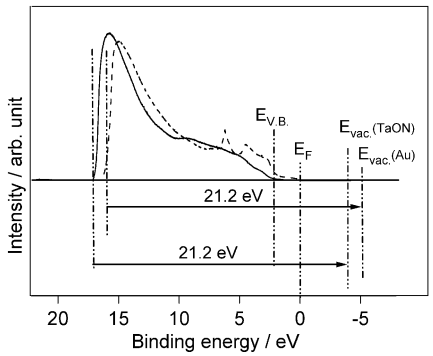

Figure 10. Comparison and relationship of E_{VB}, E_F, and E_{vac} of UPS spectra. Solid line: TaON/Pt. Dashed line: Au on TaON/Pt.

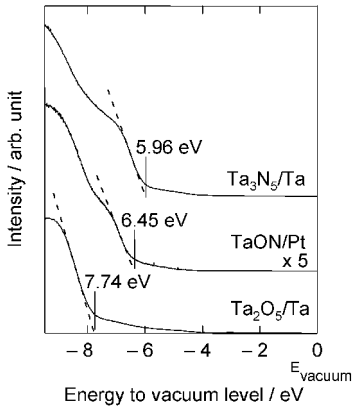

Figure 11. UPS spectra of Ta_2O_5/Ta, TaON/Pt, and Ta_3N_5/Ta in the valence band region.

function of Au is in good agreement with the literature,[15] and the estimated work functions of Au on Ta_2O_5/Ta and Ta_3N_5/Ta are the same as that of Au alone. Figure 11 shows a series of UPS spectra for Ta_2O_5/Ta, Ta_3N_5/Ta, and TaON/Pt in the valence band region. Ta_3N_5/Pt sample was prepared by electrophoretic deposition with Ta_3N_5 powder and the UPS result was coincided with the result of Ta_3N_5/Ta. (UPS spectrum of Ta_3N_5/Pt is not shown.) In this figure, the three spectra were compared with E_{vac} at the same position. The position of the top of the valence band (E_{VB}) for each sample is indicated on the spectrum. The E_{VB} positions in all measurements based on linear extrapolation are shown in Figure 11. E_{VB} shifts to lower binding energies with increasing nitrogen content in the sample. The E_{VB} and Fermi level for each sample are summarized in Table 2.

3.5. Measurement of ζ Potential. To correlate the data obtained by the two methods, the ζ potential was measured to determine the isoelectric point of each sample. The ζ potential curves against pH are shown in Figure 12. The isoelectric points of Ta_2O_5 and TaON thus determined occur at pH values of 3.3 and 2.5, respectively. For Ta_3N_5, the isoelectric point was

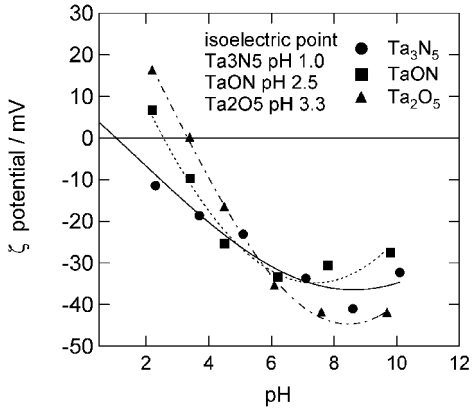

Figure 12. ζ potential vs pH curves for Ta_2O_5, TaON, and Ta_3N_5.

TABLE 2: Band Energy of Ta_2O_5/Ta, TaON/Pt, and Ta_3N_5/Ta by UPS

electrodes	Fermi level/eV	E_{VB}/eV
Ta_2O_5/Ta	−4.25	−7.74
TaON/Pt	−4.26	−6.45
Ta_3N_5/Ta	−4.15	−5.96

estimated to occur at a pH of about 1.0 by extrapolation of the ζ potential curve.

4. Discussion

The relationship between the absolute electron potential of an electrode (E_{abs}) and the standard electrode potential ($E°$) is expressed as follows.

$$E_{abs} = -E° - 4.44 \qquad \text{(at 298 K)} \qquad (2)$$

where the electron energy is 0 eV in a vacuum. This equation appears to allow correlation of the data obtained by the two methods. However, there is still uncertainty in terms of the pH to which the data obtained by UPS should be correlated. Generally, in an aqueous solution, the potential energies such as E_{CB}, E_{VB} and E_F, vary depending on the pH, particularly for oxide semiconductors. This is due to surface ionization driven by adsorbed species (e.g., H^+ and OH^-). It is considered that the net charge of the sample in UHV is zero. Therefore, the energy levels determined by UPS are assumed to correspond to those obtained in an electrolyte at the pH at which the surface charge of the sample is zero. The pH of the isoelectric points of the samples in aqueous solution was determined by measurement of the ζ potential. From Mott−Schottky plots, the E_{FB} of Ta_2O_5 and Ta_3N_5 was found to shift with pH of the solution by −60 mV per pH unit change. The E_{FB} of TaON is also expected to be a linear function of pH because the surface of TaON should behave similarly to the surfaces of Ta_2O_5 and Ta_3N_5.

On the basis of the relationship discussed above, Figure 13 illustrates the comparison of band positions determined by UPS and electrochemical measurements at pH = 0. Table 3 lists the values of E_{BG}, E_F, E_{VB}, and E_{CB} determined by UV−vis diffuse reflectance spectra, electrochemical analysis and UPS measurements. The UPS result of Ta_3N_5/Ta was coincided with the result of Ta_3N_5/Pt sample. Ta_3N_5 prepared on Ta and Ta_3N_5 powder should have the same UV−vis DR spectra. The value of E_{BG} was, therefore, determined by UV−vis DR spectra for Ta_3N_5 powder. It is generally known that the E_{CB} of many n-type semiconductors is 0.1−0.3 eV more negative than E_F.[16,17] On the basis of this, the difference is assumed to be −0.3 eV for the determination of the band positions of Ta_2O_5 and Ta_3N_5 by electrochemical measurements. The band positions determined

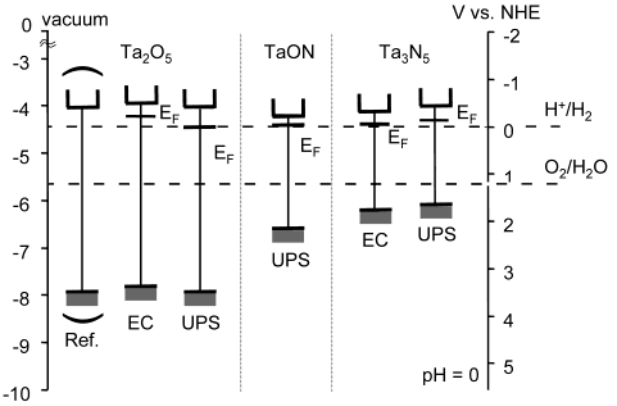

Figure 13. Band positions of Ta_2O_5, TaON, and Ta_3N_5 determined by electrochemical analysis and UPS measurements.

TABLE 3: Band Energies of Ta_2O_5, TaON, and Ta_3N_5 by Electrochemical Measurement and UPS

method	material	E_{BG}	E_F	E_{VB}	E_{CB}	ΔE^a
electrochem.	Ta_2O_5/Ta	3.9	−4.23	−7.83	−3.93	
measmt (EC)	TaON/Pt	2.4	N/A	N/A	N/A	0.3 (assumed)
at pH = 0	Ta_3N_5/Ta	2.1	−4.44	−6.02	−4.14	
UPS	Ta_2O_5/Ta	3.9	−4.45	−7.93	−4.03	−0.42
	TaON/Pt	2.4	−4.41	−6.6	−4.1	−0.21
	Ta_3N_5/Ta	2.1	−4.21	−6.02	−3.92	−0.29

[a] Difference between E_{CB} and E_F.

by the two methods for Ta_2O_5 and Ta_3N_5 are in good agreement. In addition, the band position of Ta_2O_5 determined here is consistent with electrochemical potential measurement in the literature.[18]

The difference between E_F and E_{CB} can be determined experimentally by UPS. E_F is assumed to occur at the same position as for Au deposited on the samples. Thus, the difference between E_F and E_{CB} can be determined directly. The results indicate that the assumption made for electrochemical analysis, the difference being −0.3 V, is reasonable.

Although the E_{CB} values for Ta_2O_5, TaON, and Ta_3N_5 are similar, the E_{VB} values vary significantly between these materials as shown in Figure 13. The E_{VB} values of TaON and Ta_3N_5 are at higher potential energies than that of Ta_2O_5.

The change in band positions obtained in this work is reasonably explained by density function theory (DFT) calculations.[19] DFT calculations revealed that a structure at −9 eV in UPS spectrum was attributed to O2p orbitals for TaON and Ta_2O_5. But it was suggested that some structures at around −8 eV were attributable to N2p orbitals for Ta_3N_5. The calculations of electronic band structures indicated that the valence bands of Ta_2O_5, TaON, and Ta_3N_5 consist mainly of O2p, O2p + N2p, and N2p orbitals, respectively. The conduction bands consist of Ta5d orbitals for all three materials.[19] The E_{CB} values, however, vary slightly among three samples, as shown in Figure 13. It might occur due to the difference of the crystal structures. But it is difficult to examine the detail of the difference at the present stage because the errors of UPS and electrochemical methods in our experiments are estimated to be 0.1−0.2 eV. Thus, the band gaps of an oxynitride or nitride are smaller than the corresponding oxide. These band structures are shown schematically in Figure 14.

It should be noted that all the materials studied in this work have the potential for overall water splitting. Of particular interest are TaON ($\lambda \leq 520$ nm) and Ta_3N_5 ($\lambda \leq 600$ nm), which have good absorption in the visible regime. Moreover, previous investigations of photocatalytic reactions by the present au-

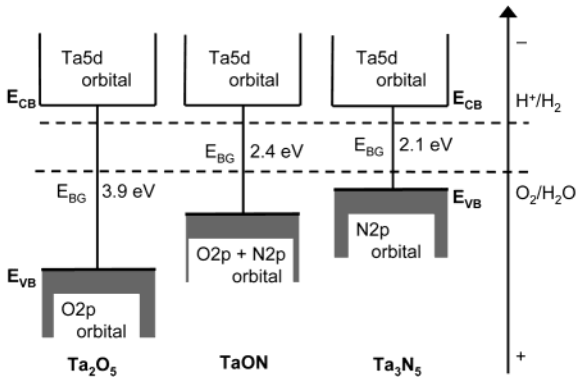

Figure 14. Schematic band structures of Ta_2O_5, TaON, and Ta_3N_5.

thors[5,6] demonstrated that TaON and Ta_3N_5 are essentially stable during photooxidation and photoreduction of water. These results indicate that this oxynitride and nitride are potential photocatalysts for overall water splitting with good visible light absorption.

5. Conclusion

The band gap positions of Ta_2O_5, TaON, and Ta_3N_5 were determined by electrochemical analysis and UPS. The conduction band positions of Ta_2O_5, TaON, and Ta_3N_5 were found to be largely similar, whereas the valence band positions vary significantly (Ta_2O_5 < TaON < Ta_3N_5). The change in the band positions is reasonably consistent with the results of DFT calculations. The results indicate that TaON and Ta_3N_5 are potential photocatalysts for overall water splitting utilizing solar radiation. Moreover, the results of UPS analysis are in good agreement with the electrochemical analysis, demonstrating that the proposed UPS technique is a reliable alternative means of determining the band positions of a wide range of photocatalytic materials.

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