Fabrication of Ta₃N₅ and ZnO Composite-Type Photoanodes by the Roll Press Method

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In our study, we fabricated Ta₃N₅ and ZnO composite-type photoanodes using the roll press method. Compared with the pristine Ta₃N₅ photoanode, the composite photoanodes exhibited better optical and photoelectrochemical properties, especially at low electrode potential. These results could have come from the high visible-light transparency of the ZnO and the formation of a heterojunction between the Ta₃N₅ and the ZnO. This fabrication process could be applied to other materials.

Key words: Photoanode, Roll press method, Ta₃N₅

1. INTRODUCTION

Since the Honda–Fujishima effect was discovered, water decomposition using photoelectrodes and sunlight gained attention as a prospective way of producing hydrogen cleanly.^{[1]–[3]} Therefore, to improve the performance of these photoelectrodes, many studies have been carried out. In fact, 10% of conversion efficiency of solar to hydrogen energy has been required for practical use.^{[2], [3]} In the previous report, a certain level of energy conversion efficiency was achieved.^{[4], [5]} On the other hand, The cost of the fabrication process and the materials has been one of the largest problems for the practical use of photoelectrochemical (PEC) water-splitting. Thus, an easy and inexpensive method is required. In our study, we focus on the other aspect of the fabrication process of photoelectrodes.

The roll press method, which is the chosen method in this study, is a way of fabricating photocatalyst films on metal substrates.^{[6], [7]} In this method, at first, any photocatalyst powder was deposited on the metal substrates by any methods (drop-cast method^[6], electrophoresis etc.), and then the pressure was put on the substrates to obtain the photocatalyst films. No necessity exists to form a special atmosphere (vacuum atmosphere, high temperature, etc.) or to use special equipment. Therefore, this method attracted our attention as one that is simple and inexpensive. Several studies using this method were reported. For example, fabrication of the Ta₃N₅/Ti photoanode is given. In this report, the Ta₃N₅ photoanode was fabricated by the roll press method for the first time, and the weak point of this method was pointed out.^[6] In another report, a different phenomenon in the dark current and the onset potential was observed on the photoelectrodes fabricated by the roll press method compared with those fabricated by the other method.^[7] This peculiar reaction detected on the photoelectrodes was also the reason why the roll press method attracted attention.

In our study, we tried to utilize the roll press method to fabricate composite-type photoelectrodes, several composite-type photoelectrodes have been reported so far.^{[8]–[10]} In this study, a heterojunction was successfully formed in the composite-type photocatalyst films.

Formation of a heterojunction can improve the PEC properties with an efficient excited charge transfer etc.^{[11]–[13]} We focus on composite-type films because fabricating them by the roll press method and obtaining the effects from the heterojunction is easy. Furthermore, mixing a photocatalyst material with another material that exhibits high visible-light transparency allows the photocatalyst particle not only on the surface but inside the film to absorb the incident light. By this phenomenon, more excited carriers are expected to be produced leading to better PEC properties.

In this study, we chose Ta₃N₅ and ZnO as the photocatalyst materials. A report exists that mentioned the ZnO@Ta₃N₅ direct Z-scheme photocatalyst.^[14] From this report, we expected that the effect from the junction of the Ta₃N₅ and the ZnO could be obtained in the composite-type photoelectrode fabricated by the roll press method.

2. EXPERIMENTAL

Ta₃N₅ was prepared by heat treatment of Ta₂O₅ (99.9%, Kojundo Chemical Lab. Co. Ltd.) under an ammonia flow. Then, 1 g of Ta₂O₅ was calcinated under NH₃ flow (flow rate: 500 mL·min⁻¹) at 850°C (programing rate: 10°C·min⁻¹) for 15 h to obtain Ta₃N₅.

The drop-cast method was also used for the deposition method. At first, Ta₃N₅ and ZnO (≥ 99.0%, Kanto Chemical co. inc., Japan) were put into 4 mL of 2-propanol. The mass ratios of Ta₃N₅/ZnO were varied, 0.67, 1.00, 2.33, 4.00, and 9.00, and the total amount of Ta₃N₅ and ZnO was 50 mg. Similarly, a 50 mg of unmixed Ta₃N₅ and ZnO was also put into 4 mL of 2-propanol. To obtain uniform dispersion, these 2-propanol containing powders were dispersed in the ultrasonic bath.

These dispersions were dropped on the Ti substrates (0.3 × 10 × 30 mm³, ≥ 99.5%, The Nilaco Corp., Japan) and then evaporated in the dryer at 80°C. This process was repeated until the <Ta₃N₅> deposition amount density reached 1.5 mg·cm⁻² (in the case of the Ta₃N₅/ZnO mass ratio = 1, the whole deposition amount was 3.0 mg·cm⁻²). Note that unmixed Ta₃N₅ and ZnO were also deposited on the Ti substrate with a deposition amount of 1.5 mg·cm⁻².

The obtained Ta_3N_5 +ZnO/Ti substrates were then pressed with rolls. The maximum load of press was approximately 15 kN. The other conditions of the roll press treatment are mentioned below; the gap between the rolls was 0.10 mm, and the roll speed was $2 \text{ m} \cdot \text{min}^{-1}$. As a comparison, the Ta_3N_5 /Ti and ZnO/Ti were pressed with rolls with 10 kN and 15 kN, respectively. After these treatments, we index the samples as Ta_3N_5 /Ti (10 or 15 kN), ZnO/Ti (10 or 15 kN), and Ta_3N_5 +ZnO/Ti ($\text{Ta}_3\text{N}_5/\text{ZnO} = 0.67, 1.00, 2.33, 4.00$, and 9.00), respectively.

Next, crystal phases of the products were determined using X-ray diffraction (XRD) on a diffractometer (Ultima IV, Rigaku Corporation, Japan) with Cu K α radiation. Surface morphologies of the Ta_3N_5 /Ti, ZnO/Ti, and Ta_3N_5 +ZnO/Ti electrodes were observed using a scanning electron microscope (SEM, VE-9800, KEYENCE Corporation, Japan), and optical properties were evaluated using ultraviolet-visible diffuse-reflectance spectroscopy (UV-vis DRS, V-650, JASCO Corporation, Japan). To evaluate the PEC properties, PEC measurements were also performed by an automatic polarization system (HSV-110, HOKUTO DENKO Corporation, Japan) in a three-electrode configuration. The cell consists of the prepared photoanode as the working electrode, an Ag/AgCl reference electrode, a Pt counter electrode, and a $0.2 \text{ M KH}_2\text{PO}_4$ ($> 99.5\%$, FUJIFILM Wako Pure Chemical Corp.) solution (pH 13, adjusted with KOH) as the electrolyte. Prior to the PEC measurements, the electrolyte was bubbled with Ar gas. The working electrodes were irradiated by AM 1.5G solar simulated light.

Electrochemical impedance spectroscopy (EIS) measurements were performed in the same three-electrode system as in the PEC measurements with the electrochemical measurements system (SP-150, Bio-logic science, France). The other conditions are given below: the range of the frequency was $0.01\text{--}1000000 \text{ Hz}$, the working electrode potential was $0.7 \text{ V}_{\text{RHE}}$, and the amplitude of the AC voltage was 10 mV .

3. RESULTS AND DISCUSSION

Fig. 1. XRD patterns of Ta_3N_5 /Ti (10 kN), ZnO/Ti (10 kN), and Ta_3N_5 +ZnO/Ti ($\text{Ta}_3\text{N}_5/\text{ZnO} = 1.00$).

Fig. 1 shows XRD patterns of the Ta_3N_5 /Ti (10 kN), ZnO/Ti (10 kN), and Ta_3N_5 +ZnO/Ti ($\text{Ta}_3\text{N}_5/\text{ZnO} = 1.00$). As shown in Fig. 1, both Ta_3N_5 and ZnO were successfully deposited on the Ti substrates. Furthermore, Fig. 2 shows XRD patterns of the Ta_3N_5 +ZnO/Ti substrates prepared by the different $\text{Ta}_3\text{N}_5/\text{ZnO}$ mass ratios. As the mass ratio was changed, the intensity of the diffraction peaks corresponded to the ZnO was increased consistently. For example, the intensity of diffraction peak at 34.5° corresponded to ZnO of Ta_3N_5 +ZnO/Ti ($\text{Ta}_3\text{N}_5/\text{ZnO} = 1.00$) was almost twice as strong as that of Ta_3N_5 +ZnO/Ti ($\text{Ta}_3\text{N}_5/\text{ZnO} = 2.33$). This suggests that the expected deposited mass ratio was achieved by the drop-cast method.

Fig. 2. XRD patterns of Ta_3N_5 +ZnO/Ti prepared by the different $\text{Ta}_3\text{N}_5/\text{ZnO}$ mass ratio (a), and enlarged view of (a) from 32 to 40 degree (b).

Fig. 3 shows the UV-vis DRS spectra of the Ta_3N_5 +ZnO/Ti with the different $\text{Ta}_3\text{N}_5/\text{ZnO}$ mass ratios. As seen in Fig. 3, the absorption bands of both Ta_3N_5 ($< 600 \text{ nm}$) and ZnO ($< 400 \text{ nm}$) were observed in the Ta_3N_5 +ZnO/Ti. However, unlike the XRD patterns, no clear tendency was confirmed for the ratio of absorption intensity of Ta_3N_5 and ZnO. These phenomena indicate the deposition of Ta_3N_5 and ZnO in a mixed state rather than a layered state.

Additionally, the absorption of the Ta_3N_5 edge was clearly confirmed, and the absorption intensity increased in the Ta_3N_5 +ZnO/Ti. Additionally, this phenomenon became more apparent when the amount of ZnO increased. Thus, this phenomenon could be from the coexistence of ZnO, which has high visible light transparency, leading to light absorption of the Ta_3N_5 particles inside the photocatalyst film.

Fig. 3. Ultraviolet-visible (UV-vis) diffuse-reflectance spectrum of $\text{Ta}_3\text{N}_5/\text{Ti}$ (10 kN), ZnO/Ti (10 kN) and $\text{Ta}_3\text{N}_5+\text{ZnO}/\text{Ti}$ prepared by the different $\text{Ta}_3\text{N}_5/\text{ZnO}$ mass ratio.

Fig. 4. Ultraviolet-visible (UV-vis) diffuse-reflectance spectrum of $\text{Ta}_3\text{N}_5/\text{Ti}$ (10, and 15 kN), ZnO/Ti (10, and 15 kN).

It is noteworthy that no apparent change existed in the absorption intensity of Ta_3N_5 between the samples prepared by the different maximum loads in the roll press treatment (10 and 15 kN) as seen in Fig. 4. Furthermore, large differences in surface morphology and roughness cannot be confirmed among $\text{Ta}_3\text{N}_5/\text{Ti}$, ZnO/Ti , and $\text{Ta}_3\text{N}_5+\text{ZnO}/\text{Ti}$ from SEM images (Fig. 5). Thus, increase in the absorption intensity of Ta_3N_5 confirmed in $\text{Ta}_3\text{N}_5+\text{ZnO}/\text{Ti}$ came from the mixed ZnO rather than from the difference in the maximum loads and the surface morphologies.

Fig. 5 SEM images of $\text{Ta}_3\text{N}_5/\text{Ti}$ (10, and 15 kN), ZnO (10, and 15 kN), and $\text{Ta}_3\text{N}_5+\text{ZnO}/\text{Ti}$ prepared by the different $\text{Ta}_3\text{N}_5/\text{ZnO}$ mass ratio.

Fig. 6 shows results of the PEC measurements for the $\text{Ta}_3\text{N}_5/\text{Ti}$ (10 kN), ZnO/Ti (10 kN), and $\text{Ta}_3\text{N}_5+\text{TaON}/\text{Ti}$. The photoanode current was observed for all photoelectrodes. Additionally, the $\text{Ta}_3\text{N}_5+\text{ZnO}/\text{Ti}$ showed a greater photocurrent than the one of $\text{Ta}_3\text{N}_5/\text{Ti}$ at a lower electrode potential (0.6–1.0 V_{RHE}). This improvement is suggested to have been from the change in optical property and the effects of the heterojunction between the Ta_3N_5 and the ZnO . Compared with the samples prepared by the other $\text{Ta}_3\text{N}_5/\text{ZnO}$ mass ratios, $\text{Ta}_3\text{N}_5+\text{ZnO}/\text{Ti}$ ($\text{Ta}_3\text{N}_5/\text{ZnO} = 1.00$) showed the greatest photocurrent at a low electrode potential as seen in Fig. 7. Considering that all the samples showed greater photocurrents than the $\text{Ta}_3\text{N}_5/\text{Ti}$, a heterojunction could successfully be formed in them all. Additionally, $\text{Ta}_3\text{N}_5+\text{TaON}/\text{Ti}$ ($\text{Ta}_3\text{N}_5/\text{ZnO} = 1.00$) showed a greater photocurrent than the other samples at lower electrode potential (0.6–1.1 V_{RHE}). This result could mainly be attributed to the optical property in this system, because the optical property of $\text{Ta}_3\text{N}_5+\text{ZnO}$ ($\text{Ta}_3\text{N}_5/\text{ZnO} = 1$) was

far superior to the other samples (Fig. 3).

Fig. 6. Current potential curves for the $\text{Ta}_3\text{N}_5/\text{Ti}$ (10 kN), ZnO/Ti (10 kN) and $\text{Ta}_3\text{N}_5+\text{ZnO}/\text{Ti}$ ($\text{Ta}_3\text{N}_5/\text{ZnO} = 1$) under the chopped light irradiation of AM 1.5G solar simulated light in a 0.2 M KH_2PO_4 solution (pH 13, adjusted with KOH).

Fig. 7. Current potential curves for the $\text{Ta}_3\text{N}_5+\text{ZnO}/\text{Ti}$ prepared by the different $\text{Ta}_3\text{N}_5/\text{ZnO}$ mass ratio under chopped light irradiation of AM 1.5G solar simulated light in 0.2 M KH_2PO_4 solution (pH 13, adjusted with KOH).

However, the photocurrent density at a high potential in the $\text{Ta}_3\text{N}_5+\text{ZnO}/\text{Ti}$ ($\text{Ta}_3\text{N}_5/\text{ZnO} = 1$) became smaller compared to the $\text{Ta}_3\text{N}_5/\text{Ti}$. This phenomenon also appeared in the $\text{Ta}_3\text{N}_5+\text{ZnO}/\text{Ti}$ ($\text{Ta}_3\text{N}_5/\text{ZnO} = 0.67$), it is suggested to be from the occurrence of the photocatalytic reaction caused by the ZnO without the combination with Ta_3N_5 when the amount of ZnO in the photocatalytic films increase. Because ZnO demonstrates a greatly inferior PEC property to pristine $\text{Ta}_3\text{N}_5/\text{Ti}$ and Ta_3N_5 demonstrates a relatively high performance at a higher potential, a decrease in the whole photocurrent density was observed. This phenomenon is also discussed in the results of the

EIS measurements. However, a large photocurrent at a lower potential was achieved. Therefore, we judged the $\text{Ta}_3\text{N}_5+\text{ZnO}$ composite-type photoelectrode to be better than the pristine Ta_3N_5 photoanode.

Fig. 8 shows the Nyquist plots obtained by the EIS measurements for $\text{Ta}_3\text{N}_5/\text{Ti}$ (10 kN), ZnO/Ti (10 kN), and $\text{Ta}_3\text{N}_5+\text{ZnO}/\text{Ti}$ prepared by the different $\text{Ta}_3\text{N}_5/\text{ZnO}$ mass ratios. In Fig. 8, the smallest semicircle was obtained in the $\text{Ta}_3\text{N}_5+\text{ZnO}/\text{Ti}$ ($\text{Ta}_3\text{N}_5/\text{ZnO} = 1$). These semicircles were attributed to the carrier transfer resistance in the photocatalyst films bulk. From these results, fabrication of the composite-type Ta_3N_5 and the ZnO photoelectrode could reduce the carrier transfer resistance, which could be attributed to the formation of a heterojunction. The EIS measurements were also performed for the $\text{Ta}_3\text{N}_5+\text{ZnO}/\text{Ti}$ fabricated by the different $\text{Ta}_3\text{N}_5/\text{ZnO}$ molar ratios. The semicircles diameters for all the $\text{Ta}_3\text{N}_5+\text{ZnO}/\text{Ti}$ were smaller than those for $\text{Ta}_3\text{N}_5/\text{Ti}$ and ZnO/Ti . This result was consistent with the results of the PEC measurements. Thus, the resistance estimated from the EIS measurements could be regarded as a clue to assume the PEC properties of this study's system.

Fig. 8. The Nyquist plots measured by the EIS measurements for the $\text{Ta}_3\text{N}_5/\text{Ti}$ (10 kN), ZnO/Ti (10 kN), and $\text{Ta}_3\text{N}_5+\text{ZnO}/\text{Ti}$ prepared by the different $\text{Ta}_3\text{N}_5/\text{ZnO}$ mass ratios under light irradiation of AM 1.5G solar simulated light in a 0.2 M KH_2PO_4 solution (pH 13, adjusted with KOH).

Finally, Fig. 9 show the Bode plot for $\text{Ta}_3\text{N}_5/\text{Ti}$ (10 kN), ZnO/Ti (10 kN), and $\text{Ta}_3\text{N}_5+\text{ZnO}/\text{Ti}$ prepared by the different $\text{Ta}_3\text{N}_5/\text{ZnO}$ mass ratio. Two peaks of phase shift at 0.1–1 Hz and 100 Hz, which are indicated by arrows (↓) in Fig. 9, were observed about $\text{Ta}_3\text{N}_5+\text{ZnO}/\text{Ti}$ ($\text{Ta}_3\text{N}_5/\text{ZnO} \leq 1$). The higher frequency phase shift peak corresponded to the peaks appearing in the ZnO/Ti . From these results, ZnO is suggested to have

caused the photocatalyst reaction without Ta_3N_5 when the $\text{Ta}_3\text{N}_5/\text{ZnO}$ mass ratio was below 1. Thus, the photocurrent density obtained from $\text{Ta}_3\text{N}_5/\text{ZnO}/\text{Ti}$ ($\text{Ta}_3\text{N}_5/\text{ZnO} \leq 1$) was the sum of the photocurrent from the Ta_3N_5 - ZnO system and only the ZnO . However, the photocurrent density observed in the ZnO was a lot smaller than the others. Thus, this phenomenon caused the decrease in the photocurrent.

As in these results, the possibility exists that both the photocatalysts caused water oxidation in the composite-type photoelectrodes, leading to a deterioration of the PEC property; so, the mixed ratio must be considered carefully.

Fig. 9. The Bode plots measured by EIS for the $\text{Ta}_3\text{N}_5/\text{Ti}$ (10 kN), ZnO/Ti (10 kN), and $\text{Ta}_3\text{N}_5+\text{TaON}/\text{Ti}$ ($\text{Ta}_3\text{N}_5/\text{ZnO} = 1$) under light irradiation of AM 1.5G solar simulated light in a 0.2 M KH_2PO_4 solution (pH 13, adjusted with KOH).

4. CONCLUSION

To summarize, we succeeded in fabricating $\text{Ta}_3\text{N}_5+\text{ZnO}/\text{Ti}$ photoanodes using the roll press method. The improvement in photocurrent compared with the pristine $\text{Ta}_3\text{N}_5/\text{Ti}$ was obtained by the composite-type photoanodes, especially at a lower potential. In other words, an improvement in the onset potential of the Ta_3N_5 photoanode was achieved. This result could have been from the formation of a heterojunction and the improvement in the optical property obtained by mixing the Ta_3N_5 and the ZnO . These results suggested that forming a heterojunction is possible by fabricating composite-type photoelectrodes using the roll press method. Additionally, mixing high transparency materials can improve the optical property. This process, and the photoelectrode structure, can be applied to some other materials.

5. REFERENCES

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