

## Ta<sub>3</sub>N<sub>5</sub> as a Novel Visible Light-Driven Photocatalyst ( $\lambda < 600$ nm)

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A transition metal nitride, Ta<sub>3</sub>N<sub>5</sub>, is a novel photocatalyst responding to visible light. Ta<sub>3</sub>N<sub>5</sub> evolves H<sub>2</sub> and O<sub>2</sub> by visible light ( $\lambda < 600$  nm) irradiation in the presence of sacrificial electron donor and acceptor, respectively without any noticeable photo-anodic or cathodic corrosion, representing a candidate for overall water splitting by visible light.

A photocatalytic system that produces clean and reproducible H<sub>2</sub> from water can be a potential method to utilize solar energy. Various kinds of photocatalysts have been found to decompose H<sub>2</sub>O to stoichiometric H<sub>2</sub> and O<sub>2</sub> under ultraviolet light irradiation.<sup>1-4</sup> Recently, In<sub>1-x</sub>Ni<sub>x</sub>TaO<sub>4</sub> was reported as a photocatalyst for water decomposition under visible light irradiation.<sup>5</sup> This catalyst, however, has only weak absorption in the visible region and the efficiency in the visible region is low. Accordingly, a satisfactory system that works under visible light irradiation has not yet been devised. Most of currently available photocatalysts for overall water splitting are metal oxides, which have wide band gaps (>3 eV), and thus only absorb ultraviolet photons.<sup>1-4</sup> The wide band gaps of such oxides are due to their deep top levels of the valence bands consisting of O<sub>2p</sub> orbitals.<sup>1</sup> Although some chalcogenides, such as CdS and CdSe, have narrower band gaps that are suitable for water splitting, they are unstable because of their photo-anodic dissolution.<sup>6,7</sup> Herein, we report a transition metal nitride, Ta<sub>3</sub>N<sub>5</sub>, as a potential candidate for a stable photocatalyst for water decomposition utilizing visible light.

Ta<sub>3</sub>N<sub>5</sub> powder was prepared from Ta<sub>2</sub>O<sub>5</sub> powder by nitridation under a flow of ammonia gas (flow rate: 1 l/min) at 1123 K for 15 h. The crystal structure of the resulting material was confirmed by XRD.<sup>8</sup> However, according to the TGA analysis, a small amount of oxygen remained after the nitridation process; the formula of the as-prepared sample was approximately Ta<sub>3</sub>N<sub>4.8</sub>O<sub>0.3</sub>. Furthermore, XPS analysis indicated that the surface contained significantly less nitrogen. For simplicity, this sample will be referred henceforth as Ta<sub>3</sub>N<sub>5</sub>. The photocatalytic reaction was carried out in a closed gas circulation system and irradiated by visible light using an Xe lamp (300 W) through a cut-off ( $\lambda > 420$  nm) and water filters to remove light in the ultraviolet and infrared regions, respectively. The catalyst (0.2 g) was suspended in an aqueous solution (200 ml) equipped with magnetic stirring. For H<sub>2</sub> or O<sub>2</sub> evolution, an aqueous methanol solution (10% v/v) or an aqueous silver nitrate solution (0.01 M) was employed as the sacrificial electron donor or acceptor, respectively. For H<sub>2</sub> evolution, Pt was loaded by the impregnation method from an aqueous Pt[(NH<sub>3</sub>)<sub>4</sub>]Cl<sub>2</sub> solution followed by H<sub>2</sub> reduction for 2 h at 573 K.

The UV-Vis diffuse reflectance spectra of Ta<sub>2</sub>O<sub>5</sub>, subjected to nitridation for various periods, are shown in Figure 1. The absorption bands in the visible region of the products increased

with longer durations of the nitridation period. As shown in Figure 1(d), heating over 10 h resulted in a Ta<sub>3</sub>N<sub>5</sub> single phase, and the band gap of Ta<sub>3</sub>N<sub>5</sub> was estimated to be 2.1 eV from its UV-Vis diffuse reflectance spectrum. It can be implied from the analogous to oxide-photocatalysts that the conduction and valence bands of Ta<sub>3</sub>N<sub>5</sub> are attributable to the Ta5d and N2p orbitals, respectively. The narrowing of the band gap by nitridation can be explained by the higher negative potential of the valence band of Ta<sub>3</sub>N<sub>5</sub> as compared to that of Ta<sub>2</sub>O<sub>5</sub><sup>9</sup>.

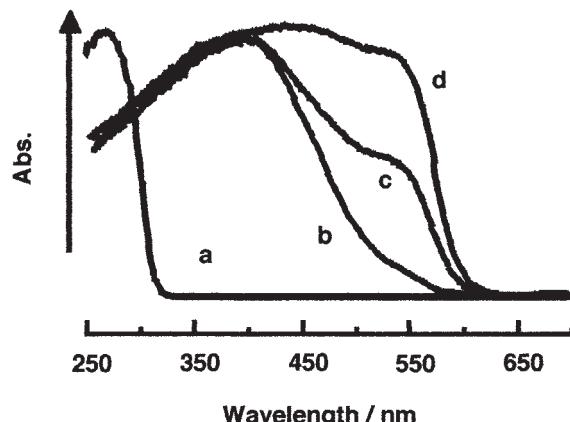
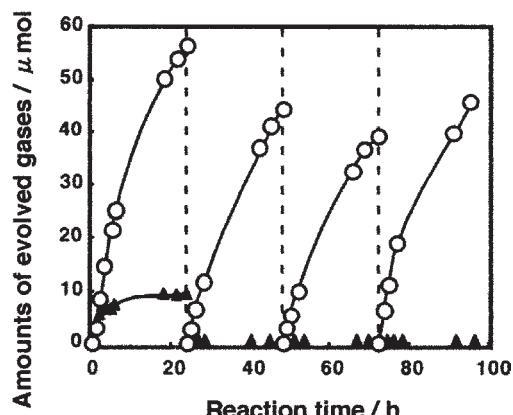


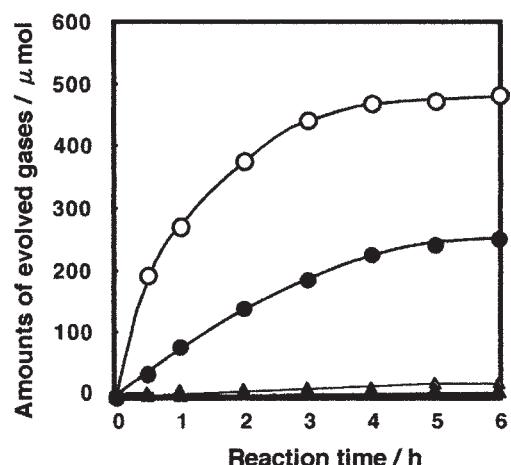
Figure 1. UV-Vis diffuse reflectance spectra of Ta<sub>2</sub>O<sub>5</sub> subjected to various durations of nitridation: (a) 0 h, (b) 1 h, (c) 5 h, (d) 10 h.

Figure 2 shows the H<sub>2</sub> evolution from an aqueous methanol solution over Pt-loaded Ta<sub>3</sub>N<sub>5</sub> catalyst (3.0% w/w) under visible light irradiation as a function of time. The reaction was conducted for 96 h, with intermediate evacuations of the products accumulated in the gas phase at 24 h intervals. Although a small amount of N<sub>2</sub> evolved in the beginning of the first run, additional N<sub>2</sub> evolution was not detected during the course of the continuous photo-irradiation. This initial N<sub>2</sub> evolution may be attributed to the oxidation of the adsorbed nitrogen-containing species and/or decomposition of the surface Ta–N species. The maintained activity of H<sub>2</sub> evolution over the long period of photo-irradiation without N<sub>2</sub> evolution indicated that degradation of the catalyst is negligible. A roughly estimated average quantum efficiency for the H<sub>2</sub> evolution between 420 nm <  $\lambda$  < 600 nm was 0.1% (based on the total photon number irradiating the reaction vessel being  $2.8 \times 10^{18}$  s<sup>-1</sup>).

Additionally, the photocatalytic activity of O<sub>2</sub> evolution on Ta<sub>3</sub>N<sub>5</sub> was examined. Figure 3 shows the O<sub>2</sub> evolution over Ta<sub>3</sub>N<sub>5</sub> catalyst from an aqueous AgNO<sub>3</sub> solution under visible light irradiation as a function of time. When the reaction was carried out in the presence of La<sub>2</sub>O<sub>3</sub> powder (0.2 g), which kept the pH value of the aqueous solution at approximately 8.5, O<sub>2</sub>



**Figure 2.**  $\text{H}_2$  (○) and  $\text{N}_2$  (▲) evolution from an aqueous methanol solution over Pt-loaded  $\text{Ta}_3\text{N}_5$ . Catalyst (0.2 g); an aqueous methanol solution (10% v/v); Pt (3.0% w/w); light source, 300 W Xe lamp ( $\lambda > 420$  nm).



**Figure 3.**  $\text{O}_2$  and  $\text{N}_2$  evolution from an aqueous  $\text{AgNO}_3$  solution over  $\text{Ta}_3\text{N}_5$  catalyst.  $\text{O}_2$  (○) and  $\text{N}_2$  (△) evolution using a mixture of  $\text{Ta}_2\text{O}_5$  and  $\text{La}_2\text{O}_3$  subjected to nitridation at 1133 K before reaction.  $\text{O}_2$  (●) and  $\text{N}_2$  (▲) evolution using  $\text{Ta}_3\text{N}_5$  and  $\text{La}_2\text{O}_3$  (simply mixed in the solution). Catalyst (0.2 g) +  $\text{La}_2\text{O}_3$  (0.2 g); aqueous  $\text{AgNO}_3$  solution (0.01 M); light source, 300 W Xe lamp ( $\lambda > 420$  nm).

evolved from the aqueous  $\text{AgNO}_3$  solution with a negligible amount of evolved  $\text{N}_2$ . However, when the reaction was carried out under acidic conditions ( $\text{pH} < \text{ca. 7}$ ), the rate of  $\text{O}_2$  evolution was remarkably suppressed, accompanied by a comparable amount of  $\text{N}_2$  evolution. The  $\text{N}_2$  evolution is attributed to the anodic-dissolution of catalyst. The oxidation of  $\text{N}^{3-}$  by valence band holes competes with the oxidation of  $\text{H}_2\text{O}$ , and the prevailing reaction is controllable by setting the pH of the reaction solution appropriately. A higher activity of  $\text{O}_2$  evolution was obtained when the  $\text{Ta}_3\text{N}_5$  catalyst was prepared by nitridation using a mixture of  $\text{Ta}_2\text{O}_5$  and  $\text{La}_2\text{O}_3$  powder. In this case, the product consisted of  $\text{Ta}_3\text{N}_5$  and unreacted  $\text{La}_2\text{O}_3$  without the formation of any other nitride or oxynitride. Figure 3 also shows the  $\text{O}_2$  evolution as a function of time using this catalyst. The initial rate of  $\text{O}_2$  evolution (ca.  $420 \mu\text{mol}/\text{h}$ ) was roughly fivefold higher than that of  $\text{Ta}_3\text{N}_5$  catalyst prepared from  $\text{Ta}_2\text{O}_5$  alone, and the  $\text{Ag}^+$  ions in the solution (2000  $\mu\text{mol}$ ) were almost entirely consumed during the photo-irradiation (6 h) to form 500  $\mu\text{mol}$  of

$\text{O}_2$ . This result also excludes the possible formation of  $\text{NO}_2^-$  or  $\text{NO}_3^-$  ions as oxidation products within our experimental error. The quantum efficiency of this reaction was estimated to be approximately 10% ( $420 \text{ nm} < \lambda < 600 \text{ nm}$ ), which is one of the highest values reported so far. The rate of  $\text{H}_2$  evolution was not enhanced as compared to that of normally prepared  $\text{Ta}_3\text{N}_5$  catalyst.

Based on these results,  $\text{Ta}_3\text{N}_5$  has a band structure available for both the reduction of  $\text{H}^+$  and oxidation of water. Although some photocatalysts such as  $\text{WO}_3$  and  $\text{BiVO}_4$  have shown  $\text{O}_2$  evolution from  $\text{AgNO}_3$  solution under visible light irradiation, such materials have not exhibited reduction of  $\text{H}^+$  into  $\text{H}_2$  because their conduction bands do not have sufficient potentials for  $\text{H}_2$  evolution.<sup>10</sup> Our preliminary photoelectrochemical measurements using a  $\text{Ta}_3\text{N}_5$  film formed on Ta metal foil indicated that the flat band potential of  $\text{Ta}_3\text{N}_5$  is about  $-0.1 \text{ eV}$  (vs NHE, at  $\text{pH} = 6$ ). Moreover,  $\text{Ta}_3\text{N}_5$  was found to be of an *n*-type semiconductor, and presumably the bottom of its conduction band is located at a more negative potential of about  $0.2 \text{ eV}$  than the flat band potential. The top level of the valence band is estimated to be about  $1.8 \text{ eV}$  (vs NHE).

The high efficiency of  $\text{O}_2$  evolution from aqueous  $\text{AgNO}_3$  solution indicates the facile migration of electrons and holes in the bulk of  $\text{Ta}_3\text{N}_5$  to the surface. The difficulty to enhance the activity of  $\text{H}_2$  evolution may be due to the presence of surface states trapping photo-generated electrons, which are favorable in reducing  $\text{Ag}^+$  ions but unfavorable for  $\text{H}_2$  evolution. This suggestion is supported by the TGA and XPS analyses indicating surface imperfection as mentioned above. Therefore, the rate-determining step of  $\text{H}_2$  evolution is considered to be the electron transfer to Pt or to  $\text{H}^+$  on the surface of the catalyst. The rate of  $\text{H}_2$  evolution from aqueous methanol solution could be enhanced if the electron transfer from  $\text{Ta}_3\text{N}_5$  to the loaded Pt particles or  $\text{H}^+$  ions is facilitated.

In summary, a transition metal nitride,  $\text{Ta}_3\text{N}_5$ , was presented as a novel photocatalyst that has a potential to evolve  $\text{H}_2$  and  $\text{O}_2$  under visible light irradiation. The photocatalytic activity of  $\text{Ta}_3\text{N}_5$  was relatively high for  $\text{O}_2$  evolution from aqueous  $\text{AgNO}_3$  solution, reaching quantum efficiency of 10%, but was relatively low for  $\text{H}_2$  evolution (ca. 0.1%). Another important result is that photo-anodic or cathodic corrosion was prevented in alkaline solutions, which is distinctively different than previously examined photocatalysts with narrow band gaps such as some chalcogenides. Because  $\text{Ta}_3\text{N}_5$  is a promising candidate for overall water-splitting utilizing visible light, we are presently attempting to improve the activity for  $\text{H}_2$  evolution.

#### References and Notes

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