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TaON and Ta_3N_5 as new visible light driven photocatalysts

Michikazu Hara [a], Go Hitoki [a], Tsuyoshi Takata [a], Junko N. Kondo [a],
Hisayoshi Kobayashi [b], Kazunari Domen [a,c,*]

[a] *Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan*
[b] *Department of Chemical Technology, College of Science and Industrial Technology, Kurashiki University of Science and the Arts, 2640 Nishinoura, Tsurajima-cho, Kurashiki 712-8505, Japan*
[c] *Core Research for Evolutional Science and Technology, Japan Science and Technology Co. (CREST, JST), 2-1-13 Higashi-ueno, Daito-ku 110-0015, Japan*

Abstract

TaON and Ta_3N_5, Ta^{5+}-based (oxy)nitrides, were studied as visible light driven photocatalysts. Under visible light irradiation ($\lambda \geq 420$ nm), the (oxy)nitrides oxidize water to O_2 and reduce H^+ to H_2 in the presence of sacrificial reagents (Ag^+ and methanol). TaON oxidizes water into O_2 efficiently, with a maximum quantum yield of 10%. The photocatalytic reactions proceed via the bandgap transitions (E_g, TaON: 2.5 eV, Ta_3N_5: 2.1 eV) without any noticeable degradation of the catalysts. The small energy gaps of TaON and Ta_3N_5 are ascribed to the valence band structures consisting of N 2p orbitals.

Keywords: TaON; Ta_3N_5; Photocatalysts

1. Introduction

In order to satisfy energy conservation requirements and the increasingly stringent standards of environmental regulations, catalytic techniques are being applied in various fields. Photocatalysis is one technique that has great potential for the conversion of photon energy into chemical energy and to decompose pollutants in air or solution. Any photocatalyst that functions in visible light would have genuine applications in solar energy utilization.

(Oxy)nitrides containing Ta^{5+} or Ti^{4+}, such as TaON, Ta_3N_5 and $LaTiO_2N$, are potential visible light driven photocatalysts. These stable inorganic pigments are synthesized without difficulty by nitriding metal oxides under NH_3 flow, and have been demonstrated to absorb visible light at 500–650 nm [1–3]. In addition, these (oxy)nitrides are not toxic, in contrast to CdS and CdSe. Density functional theory (DFT) calculations for TaON and Ta_3N_5 show that these materials have the following common features [4]. First, the formal electronic configurations of transition metal cations are d^0. Second, the bottoms of the conduction bands consist of the empty d orbitals, and the tops of the valence bands mainly consist of N 2p orbitals. As a result, the band structures are essentially similar to those of d^0-transition metal oxide photocatalysts such as TiO_2, $SrTiO_3$, $K_4Nb_6O_{17}$ and $NaTaO_3$ [5–7]. These metal oxides function as stable and efficient photocatalysts under ultraviolet irradiation, and the conduction and valence bands are composed of empty transition metal d orbitals and O 2p orbitals, respectively.

In this paper, we report photocatalytic reactions by TaON and Ta_3N_5 under visible light. The schematic

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* Corresponding author. Tel.: +81-45-924-5239.
E-mail address: mhara@res.titech.ac.jp (M. Hara).

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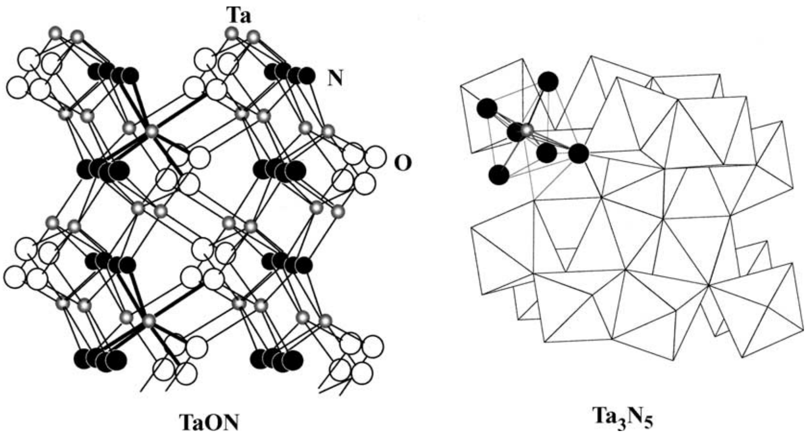

Fig. 1. Schematic structures of TaON and Ta_3N_5.

structures of TaON and Ta_3N_5 are illustrated in Fig. 1. β-TaON is a yellow to yellowish-green oxynitride that has the same structure as baddeleyite, monoclinic ZrO_2 [2]. The structure of Ta_3N_5 consists of TaN_6 octahedra and is similar to Ti_3O_5 (ansovite) [1].

2. Experimental

2.1. Syntheses of TaON and Ta_3N_5

TaON and Ta_3N_5 were prepared by heating Ta_2O_5 powder (Rare Metallic, purity: 99.9%) in an alumina tube reactor under a flow of ammonia gas (flow rate: 20–1000 $cm^3\,min^{-1}$) at 1123 K for 15 h. The nitriding reactor was directly connected to a silicon oil bubbler made of Pyrex, and the effluent gas with entrained water generated during nitriding was passed into the bubbler at 420 K, preventing contamination by water and O_2 in air.

2.2. Photocatalytic reactions

The reaction was carried out in a Pyrex reaction vessel connected to a closed gas circulation and evacuation system. Photoreduction of H^+ to H_2 and photooxidation of H_2O to O_2 in the presence of a sacrificial electron donor (methanol) and acceptor (Ag^+) were examined as test photoreactions. H_2 evolution was examined in an aqueous solution (200 ml) containing 0.20–0.40 g of the sample loaded with 3 wt.% Pt and 20 ml of methanol as a sacrificial donor. In the case of typical photooxidation of water into O_2, the reaction was performed in an aqueous $AgNO_3$ solution (0.01–0.05 M; 200 ml) containing 0.20–0.40 g of the catalyst and 0.20 g of La_2O_3 powder. La_2O_3, a basic oxide, was added to maintain the pH of the solution at around 8 during the reaction (see below). The reaction solution vessel was evacuated several times to remove air and the solution was then irradiation with a 300 W Xe lamp equipped with cut-off filters. The evolved gas was then extracted and analyzed by gas chromatography.

Quantum efficiencies (QEs) were calculated using the equation: $\text{QE}\ (\%) = (AR/I) \times 100$, where A, R, and I are coefficients based on the reactions (H_2 evolution: 1, O_2 evolution: 4), the H_2 or O_2 evolution rate (molecules h^{-1}) and the rate of absorption of incident photons ($420 \leq \lambda \leq 600$ nm: 9.6×10^{21} photons h^{-1}; $420 \leq \lambda \leq 500$ nm: 4.2×10^{21} photons h^{-1}), respectively.

3. Results and discussion

3.1. XRD patterns and UV-Vis diffuse reflectance spectra of TaON and Ta_3N_5

Fig. 2 shows X-ray diffraction (XRD) patterns of Ta_2O_5 and the prepared samples (NH_3 flow rate: 20 and 1000 $cm^3\,min^{-1}$). Nitriding of Ta_2O_5 at the flow rate of 20 $cm^3\,min^{-1}$ resulted in the production of a

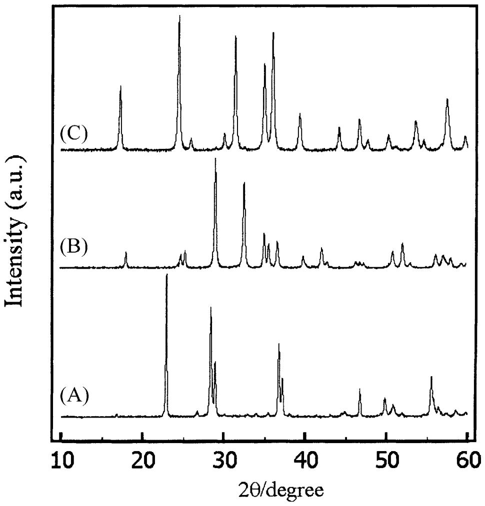

Fig. 2. XRD patterns of: (A) Ta_2O_5; (B) sample prepared under NH_3 flow at 20 $cm^{-3}\,min^{-1}$; (C) sample prepared under NH_3 flow at 1000 $cm^{-3}\,min^{-1}$.

yellow powder, and in the case of 1000 $cm^3\,min^{-1}$, a scarlet powder. The XRD patterns correspond to those of β-TaON and Ta_3N_5 in the literature, respectively [1,2]. No impurity phase was observed in the XRD patterns, and elemental analysis revealed that the compositions of both samples were $TaO_{1.3}N_{0.8}$ and $Ta_3O_{0.3}N_{4.8}$, respectively. This indicates that the prepared TaON and Ta_3N_5 are nonstoichiometric and defective.

UV-Vis diffuse reflectance spectra of TaON, Ta_3N_5 and Ta_2O_5 are shown in Fig. 3. The absorption band-edge of TaON is ca. 500 nm, shifted about 170 nm from that of Ta_2O_5, and the bandgap energy was estimated to be 2.5 eV. Ta_3N_5 has a broader absorption edge (600 nm) and smaller energy gap (2.1 eV) than TaON. It can be inferred from analogous oxide photocatalysts that the conduction and valence bands of TaON and Ta_3N_5 are attributable to the Ta 5d and N 2p orbitals, respectively. Because N 2p orbitals have higher potential energies than O 2p, the increase in N results in the higher negative potential of the valence band compared to that of Ta_2O_5 and the narrowing of the energy gap.

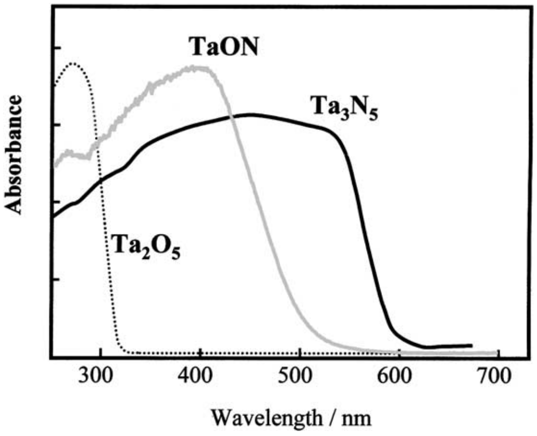

Fig. 3. UV-Vis diffuse reflectance spectra of Ta_2O_5, TaON and Ta_3N_5.

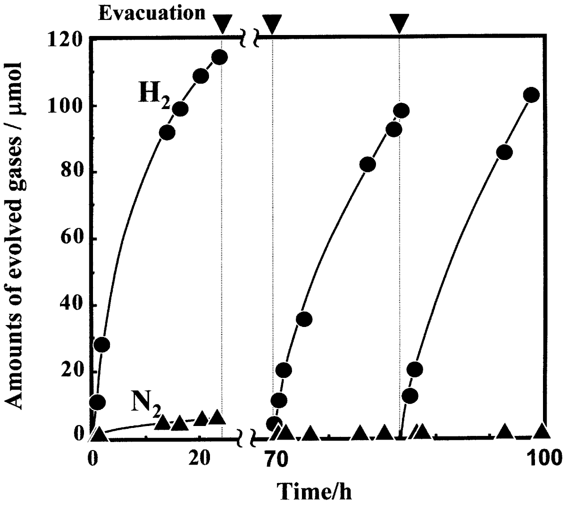

Fig. 4. H_2 evolution by Pt-deposited TaON under visible light (λ ≥ 420 nm). The 0.4 g TaON, 200 ml of 20 vol.% aqueous methanol solution.

3.2. *Photocatalytic reaction of TaON and Ta_3N_5*

Time course of H_2 evolution by TaON under visible light (λ ≥ 420 nm) and optimal conditions (TaON: 0.4 g) is shown in Fig. 4. No reaction took place in the dark. H_2 evolution occurred as a result of the reduction of H^+ to H_2 by excited electrons in TaON. The initial quantum efficiency for H_2 evolution in the first reaction was estimated to be about 0.10%.[1] In subsequent reactions after repeated evacuation, H_2 evolution

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[1] Quantum efficiencies in TaON and Ta_3N_5 were calculated on the basis of the rates of absorption of incident photons at 420 ≤ λ ≤ 500 nm and 420 ≤ λ ≤ 600 nm, respectively, because TaON and Ta_3N_5 did not function at λ > 500 and 600 nm, respectively.

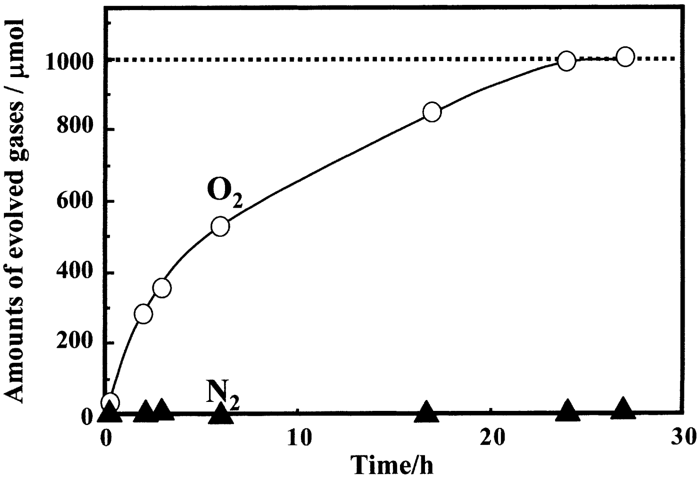

Fig. 5. O_2 evolution by TaON under visible light ($\lambda \geq 420$ nm). TaON: 0.4 g, La_2O_3: 0.2 g, 200 ml 0.02 M $AgNO_3$ solution.

proceeded without a significant decrease in activity, indicating that TaON functions as a photocatalyst for photoreduction of H^+ into H_2 under visible light irradiation. N_2 evolution was observed in the early stage of the first reaction, and 4.8 µmol of N_2 was detected in the first run. This can be attributed to an oxidation product of TaON itself:

$$2N^{3-} + 6h^{-} \rightarrow N_2$$

However, N_2 was not detected at all by gas chromatography after the second run. Therefore, the catalyst is considered to be stable during the reaction.

Fig. 5 shows time course of O_2 evolution by TaON under visible light ($\lambda > 420$ nm) irradiation. Upon optimal conditions ($AgNO_3$ solution: 0.02 M, TaON: 0.4 g), efficient O_2 evolution began at an initial rate of 200 µmol h^{-1}, corresponding to a quantum yield of 10% (see footnote 1). In this case, N_2 evolution due to oxidation of TaON was not observed. The rate of O_2 evolution decreased with reaction time due to the decrease of Ag^+ concentration and coverage of the TaON surface with metallic Ag particles that obstructed photon absorption. The total amount of evolved O_2 (1000 µmol) corresponds closely to the amount that can be evolved by the stoichiometric reduction of Ag^+ (Ag^+: 4000 µmol, O_2: 1000 µmol). No difference in the XRD patterns of the catalyst from the fresh state was observed after the reaction except for the presence of Ag. These results indicate that TaON oxidizes water into O_2 as a stable visible light driven photocatalyst.

The relationships between the H_2 and O_2 evolution rates and the cut-off wavelength of incident light are shown in Fig. 6. H_2 and O_2 evolution were examined in aqueous solutions containing methanol or $AgNO_3$ as described above, and the rates were obtained in the early stages of the reactions (1–2 h). The rate of H_2 or O_2 evolution decreases with increasing cut-off wavelength, and the longest wavelength that supported

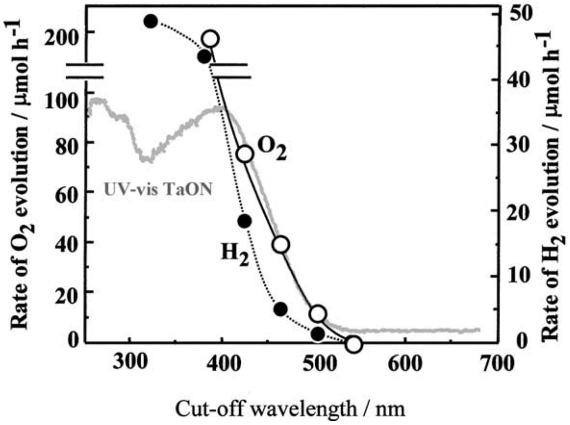

Fig. 6. Dependence of initial rates of H_2 and O_2 on cut-off wavelength of incident light, and UV-Vis DR spectrum of TaON. H_2: 0.4 g Pt-deposited TaON treated with 20 vol.% aqueous methanol solution, O_2: 0.4 g TaON, 0.2 g La_2O_3, 0.02 M $AgNO_3$ solution.

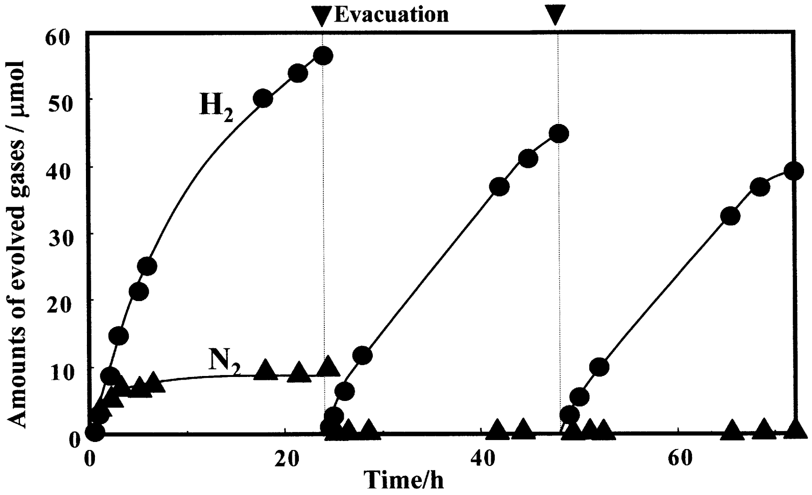

Fig. 7. H_2 evolution by Ta_3N_5 under visible light ($\lambda \geq 420$ nm). The 0.2 g Pt-deposited Ta_3N_5, 200 ml 20 vol.% aqueous methanol solution.

either photoreaction was estimated to be ca. 500 nm. This corresponds to the absorption edge of TaON. As a result, these photoreactions are considered to proceed via bandgap transition.

Figs. 7 and 8 show the progress of H_2 and O_2 evolution from Ta_3N_5 under visible light ($\lambda \geq 420$ nm) irradiation, respectively. These reactions were performed under optimal conditions (H_2 evolution: Pt-deposited Ta_3N_5 (0.2 g)–20 vol.% aqueous methanol solution, O_2 evolution: Ta_3N_5 (0.2 g)–La_2O_3(0.2 g)–0.01 M $AgNO_3$ solution). Under visible light, Ta_3N_5 reduces H^+ into H_2 or oxidizes water into O_2 in the presence of sacrificial reagents via bandgap transition (2.1 eV) because the longest wavelength that supported either photoreaction was estimated to be ca. 600 nm, corresponding to the absorption edge of Ta_3N_5. The maximum quantum yields ($\lambda \geq 420$ nm) for H_2 and O_2 evolution were 0.06 and 10%, respectively (see footnote 1). In the early stages of both reactions (1–2 h), small amounts of N_2 evolution were observed as shown in Figs. 7 and 8, however, it was confirmed that further degradation of Ta_3N_5 did not proceed. Ta_3N_5 therefore appears to function as a stable photocatalyst for reduction of H^+ or oxidation of water under visible light irradiation as well as TaON.

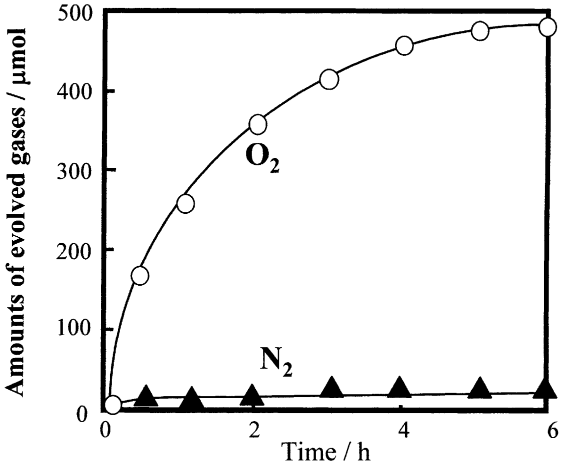

Fig. 8. O_2 evolution by Ta_3N_5 under visible light ($\lambda \geq 420$ nm). The 0.2 g Ta_3N_5, 0.2 g La_2O_3, 200 ml 0.01 M $AgNO_3$ solution.

As mentioned before, the compositions of the above TaON and Ta_3N_5 obtained by nitriding for 15 h were estimated to be were $TaO_{1.3}N_{0.8}$ and $Ta_3O_{0.3}N_{4.8}$, respectively. When TaON and Ta_3N_5 samples were prepared by nitriding for 13–17 h, it was confirmed that the compositions of obtained TaON and Ta_3N_5 samples were $TaO_{1.5}N_{0.7} \sim TaO_{1.0}N_{1.0}$ and $Ta_3O_{0.5}N_{4.7} \sim Ta_3O_{0.1}N_{4.9}$, respectively. In both cases, the amounts of oxygen in the samples decreased with increasing nitriding time, and it is expected that the amounts of defects also change with the alteration of the compositions. On the other hand, there was no difference in UV-Vis diffuse reflectance spectrum and XRD pattern among TaON or Ta_3N_5 samples. In addition, these TaON or Ta_3N_5 samples showed the same photocatalytic activities despite the differences in the composition and defect. This suggests that that the visible light responsive properties of these catalysts depend largely on the structures of TaON and Ta_3N_5, rather than nonstoichiometric and/or defective nature of these materials.

It is noteworthy that O_2 evolution from TaON and Ta_3N_5 depends largely on pH. O_2 evolution was examined in a basic solution (ca. pH 8) buffered by La_2O_3 as described above. However, when the reaction was carried out under relatively acidic conditions (pH ca. <7), the rate of O_2 evolution was remarkably suppressed, accompanied by a comparable amount of N_2 evolution. This implies that alkaline conditions are favorable for oxidation of water by TaON and Ta_3N_5.

To summarize the results, TaON and Ta_3N_5 are stable visible light driven photocatalysts with good reduction and oxidation potentials. The bottoms of the conduction bands are more negative than the reduction potential of H^+, and the tops of the valence bands are more positive than the oxidation potential of water. This suggests that these (oxy)nitrides are useful visible light driven photocatalysts for the cleavage of water. However, at present, neither photocatalyst can be used for overall photocatalytic water splitting because of the low rates of H_2 evolution. It is very important for the cleavage of water by photocatalysts to separate exited electrons and generated holes efficiently, and H_2 evolution promoters on photocatalysts play an important role in efficient charge separation. Pt-deposited TaON and Ta_3N_5 do not have high photocatalytic activities for H_2 evolution, meaning that efficient charge separation does not proceed on these Pt-deposited photocatalysts. Improvement of activity for H_2 evolution is currently under investigation for photocatalytic overall water splitting in visible light.

4. Conclusion

TaON and Ta_3N_5 synthesized by nitriding Ta_2O_5 have small bandgap energies (TaON: 2.5 eV, Ta_3N_5: 2.1 eV) and absorb visible light at 500–600 nm via the N 2p orbitals of the tops of the valence bands. Under visible light irradiation, these (oxy)nitrides reduce H^+ into H_2 or oxidize water into O_2 in the presence of a sacrificial electron donor or acceptor without significant degradation of the materials, indicating that these materials are stable visible light driven photocatalysts with good reduction and oxidation potentials. TaON and Ta_3N_5 oxidize water into O_2 efficiently, with maximum quantum yields of 10%.

Acknowledgements

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