

An oxynitride, TaON, as an efficient water oxidation photocatalyst under visible light irradiation ($\lambda \leq 500$ nm)

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Under visible light irradiation ($\lambda = 420\text{--}500$ nm), a tantalum oxynitride, TaON, functions as a stable and very efficient photocatalyst for oxidation of water into O₂ with a sacrificial electron acceptor (Ag⁺).

Many oxide photocatalysts have been developed for energy problem and the increasingly stringent standards of environmental regulations.^{1,2} Among these, Ta₂O₅ and some tantalates such as NaTaO₃ work as highly active photocatalysts and can even decompose water efficiently, with proper modification.³ Most of these tantalum oxides have band gap energies that are too large to efficiently use solar radiation, however. In these Ta⁵⁺-based oxides, the valence bands predominantly consist of O 2p orbitals whose potential energy levels are located at a deep position of about 3 V vs. NHE (or about -7.44 V vs. vacuum level)⁴ Due to this fact, it is generally not feasible to find a transition metal oxide photocatalyst that functions under visible light irradiation. Although NiO-modified InTaO₄ was recently reported as an effective photocatalyst for water splitting under visible light irradiation,⁵ the absorption in the visible light region was not significant and the photocatalytic efficiency was very low.

Recently, we have been studying early transition metal (oxy)nitrides as photocatalysts. (Oxy)nitrides containing Ti⁴⁺, Nb⁵⁺ and Ta⁵⁺ have reasonable absorption in the visible light region, *i.e.* the absorption edges are at 500–650 nm, corresponding to band gap energies of 1.9–2.5 eV. Interestingly, some of these materials show activity for water oxidation as well as reduction under visible light irradiation ($\lambda \geq 420$ nm), and they are essentially stable during the photoreactions. In this communication, we report the photocatalytic behavior of one such oxynitride, TaON, because it shows very high activity for water oxidation under visible light irradiation.

β -TaON is a yellow–yellowish-green oxynitride that has the same structure as baddeleyite, monoclinic ZrO₂.⁶ From the band structure of β -TaON, as calculated by density functional theory (DFT),⁷ the bottom of the conduction band is based on empty Ta 5d orbitals similar to Ta₂O₅, whereas the top of the valence band consists of a hybridization of N 2p and O 2p orbitals in which the N 2p contribution is larger than that of O 2p. The potential energy of the hybridized orbital is higher than that of an O 2p orbital in an oxide, resulting in a smaller band gap energy sufficient to absorb visible light.

TaON was prepared by heating Ta₂O₅ powder in an atmosphere of flowing NH₃ (flow rate: 20 ml min⁻¹) at 1123 K for 15 h. The X-ray diffraction (XRD) pattern (data not shown) coincided with that of β -TaON in the literature.⁶ Fig. 1 shows UV–visible diffuse reflectance spectra of TaON and Ta₂O₅. The absorption band-edge of TaON is at *ca.* 500 nm, being shifted by about 170 nm from that of Ta₂O₅, and the band gap energy was estimated to be 2.5 eV. Elemental analysis revealed that the composition of the sample was TaO_{1.24}N_{0.84}, indicating that the prepared ‘TaON’ was nonstoichiometric and defective.

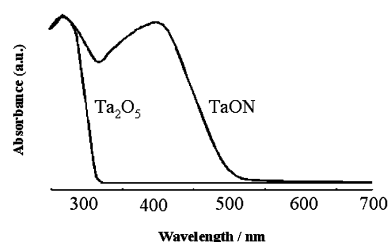


Fig. 1 UV–visible diffuse reflectance spectra of TaON and Ta₂O₅.

Photooxidation of H₂O into O₂ and photoreduction of H⁺ into H₂ were used as test reactions to evaluate the photocatalytic capabilities of TaON. The reactions were carried out in a Pyrex reaction vessel connected to a closed gas circulation system constructed of glass. For the photooxidation of water into O₂, the reaction was performed in an aqueous AgNO₃ solution (0.01 M; 200 ml) containing 0.40 g of the TaON catalyst and 0.2 g of La₂O₃ powder. The La₂O₃, a basic oxide, was added to maintain the pH of the solution at around 8 during the reaction. The H₂ evolution was examined in an aqueous solution (200 ml) containing 0.40 g of TaON loaded with 3 wt% Pt, and 20 ml of methanol as a sacrificial donor. The reaction solution was evacuated several times to remove air, followed by irradiation with a 300 W Xe lamp equipped with a cut-off filter ($\lambda = 420$ nm). The evolved gas was analyzed by gas chromatography.

Fig. 2 shows the time course of O₂ evolution under visible light ($\lambda > 420$ nm) irradiation. No reaction took place in the dark. Upon visible light irradiation, O₂ evolution started and the initial rate was 660 $\mu\text{mol h}^{-1}$, which corresponds to a quantum yield of 34%.[†] The rate of O₂ evolution decreased with reaction time due to the decrease in Ag⁺ concentration and because the surface of TaON became covered with metallic Ag particles that obstructed photon absorption into the TaON. The total amount of evolved O₂ (500 μmol) corresponds closely to the amount

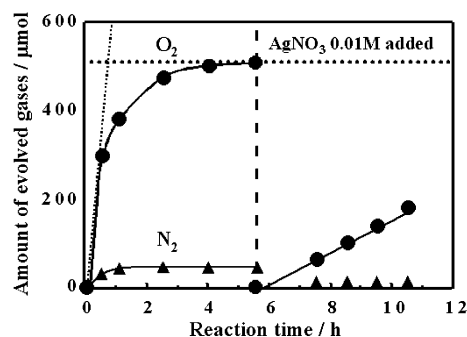


Fig. 2 Time course of O₂ (●) evolution from TaON under visible light irradiation ($\lambda > 420$ nm). TaON: 0.4 g, La₂O₃: 0.2 g, 200 mL 0.01 M AgNO₃ solution.

that can be evolved by the stoichiometric reduction of Ag^+ (Ag^+ : 2000 μmol , O_2 : 500 μmol). It was confirmed by XRD, X-ray photoelectron spectroscopy (XPS) and inductive coupling plasma (ICP) analysis that after the reaction for 5.5 h, all Ag^+ in the solution was deposited on TaON as metallic Ag^0 . There was no difference in the XRD patterns of the catalyst before and after the reaction except for the presence of Ag metal. In the early stage of the reaction (first 1–2 h), a small amount of N_2 evolution was detected. This was attributed to the oxidation of N^{3-} in the TaON into N_2 . However, the amount of N_2 from assumed photogenerated holes corresponded to less than 1% of the catalyst, and further degradation of TaON did not occur. Actually, in the second run after another AgNO_3 (2000 μmol) addition, no N_2 evolution was observed. The slower rate of O_2 evolution was due to Ag metal deposition on TaON. O_2 evolution under visible light irradiation was also observed in a $\text{Na}_2\text{S}_2\text{O}_8\text{--Na}_2\text{SO}_4$ ($\text{Na}_2\text{S}_2\text{O}_8$: 1.0×10^{-2} M, Na_2SO_4 : 5.0×10^{-2} M, 200 ml) aqueous solution containing TaON although the rates of O_2 evolution was *ca.* 1/4 that of AgNO_3 . This indicates that TaON in visible light functions as a photocatalyst for oxidation of water even in the presence of $\text{S}_2\text{O}_8^{2-}$ as an electron acceptor.

The time course of H_2 evolution on TaON in visible light ($\lambda > 420$ nm) is shown in Fig. 3. H_2 evolution occurred as a result of the reduction of H^+ to H_2 by excited electrons in TaON. Simultaneous evolution of CO_2 due to the oxidation of methanol was also confirmed. After evacuation of the solution, H_2 evolution proceeded without any decrease in activity, indicating that TaON also functions as a photocatalyst for photoreduction of H^+ into H_2 under visible light irradiation. The estimated quantum efficiency was *ca.* 0.2%, which was much lower than that of the water oxidation. Although a very small level of N_2 evolution was observed in the early stage of the reaction, N_2 did not evolve during subsequent reactions. This indicates that TaON is essentially stable during the H_2 evolution reaction.

Fig. 4 shows the dependence of the H_2 or O_2 evolution rates on the cut-off wavelength of the incident light. The rates were determined in the early stages of the reactions (first 1–2 h). The rates of both H_2 and O_2 evolution decreased with increasing cut-off wavelength, and the longest wavelength available for both photoreactions was estimated to be *ca.* 500 nm. This corresponds to the absorption edge of TaON. As a result, these photoreactions are considered to proceed by the bandgap transition.

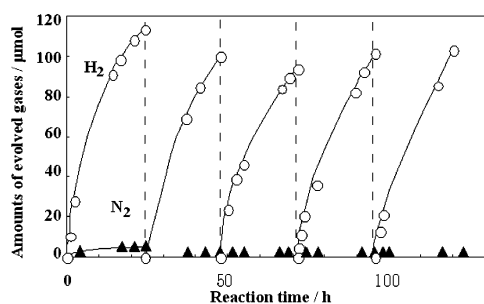


Fig. 3 Time course of H_2 evolution (\circ) from TaON under visible light irradiation ($\lambda > 420$ nm). Pt-deposited TaON: 0.4 g, 200 mL methanol solution (distilled water 180 mL, methanol 20 mL).

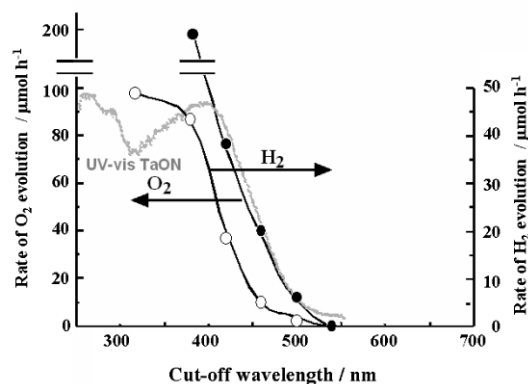


Fig. 4 Dependence of the initial rates of H_2 (\circ) and O_2 (\bullet) evolution on the cut-off wavelength of incident light, and UV–visible diffuse reflectance spectrum of TaON. H_2 and O_2 evolution were examined with a Pt-deposited TaON (0.4 g), 10 vol% aqueous methanol solution and a TaON (0.4 g), La_2O_3 (0.2 g), 0.01 M AgNO_3 solution system, respectively.

In summary, TaON was found to be a novel visible light-driven photocatalyst. Especially, photooxidation of water on TaON proceeded very efficiently. On the other hand, the photocatalytic activity for H_2 evolution was not high. By both of electrochemical analysis and UV photoelectron spectroscopy for the TaON film, the bottom of the conduction band and the top of the valence band were estimated to be *ca.* -0.3 and 2.2 V vs. NHE at pH 0, respectively, suggesting that TaON has a sufficient potential for reduction of H^+ in spite of the small H_2 evolution. This is currently under investigation. The details will be published soon.

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Notes and references

† Quantum efficiencies (F) were calculated using the following equation: $F(\%) = (AR/I) \times 100$, where A represents the coefficient based on the reaction (for H_2 evolution: 1; for O_2 evolution: 4), R represents the H_2 or O_2 evolution rate (molecules h^{-1}), and I represents the rate of absorption of incident photons (9.6×10^{21} photons h^{-1} at $\lambda = 420\text{--}500$ nm). We assumed that visible light at $\lambda < 500$ nm was available for the photoreactions because TaON did not work at $\lambda > 500$ nm, as shown in Fig. 4.

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