

Enhanced Water Oxidation on Ta₃N₅ Photocatalysts by Modification with Alkaline Metal Salts

Su Su Khine Ma,[†] Takashi Hisatomi,[†] Kazuhiko Maeda,^{†,‡,§} Yosuke Moriya,[†] and Kazunari Domen^{*,†}

[†]Department of Chemical System Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

[‡]Precursory Research for Embryonic Science and Technology (PRESTO), Japan Science and Technology Agency (JST), 4-1-8 Honcho Kawaguchi, Saitama 332-0012, Japan

S Supporting Information

ABSTRACT: Tantalum nitride (Ta₃N₅) is a promising nitride semiconductor photocatalyst for solar water splitting because it has band edge potentials capable of producing hydrogen and oxygen from water under visible light ($\lambda < 590$ nm). However, the photocatalytic performance of Ta₃N₅ has been far below expectations because insufficient crystallization upon thermal nitridation of the oxide precursors enhances undesirable charge recombination limiting the quantum efficiency of the photocatalytic reaction. This problem was successfully rectified in this study by modifying the surface of the starting Ta₂O₅ with a small amount of alkaline metal (AM) salts. Compared with conventional Ta₃N₅, Ta₃N₅ nitrided from AM salt-modified Ta₂O₅ had better crystallinity and smaller particles with smoother surfaces and, most importantly, demonstrated a 6-fold improvement in photocatalytic activity for O₂ evolution under visible light. AM salt modification was compatible with the loading of an O₂ evolution cocatalyst, such as CoO_x, yielding an apparent quantum efficiency of 5.2% at 500–600 nm. This indicates that the effects of AM modification were attributable to the changes in the crystallinity and the morphology of Ta₃N₅ rather than to catalytic effects. Detailed characterization of the Na₂CO₃-modified Ta₃N₅ suggested partial dissolution of Ta₂O₅ and nucleation of NaTaO₃ in the early stages of nitridation, which gave rise to the characteristic particle morphologies and improved the crystallinity of the nitridation products. This study demonstrates that a facile pretreatment of a starting material can improve the physical and photocatalytic properties of photocatalysts drastically, enabling the development of advanced photocatalysts for solar water splitting.

Photocatalytic water splitting may provide an economically viable approach to the direct conversion of solar energy into renewable and storable hydrogen and oxygen, since both water and sunlight are naturally abundant. Due to its simplicity, water splitting using a powdered photocatalyst has stimulated great interest, especially with a focus on visible light responsive photocatalysts for effective utilization of sunlight.¹ Tantalum nitride (Ta₃N₅) is one of the most promising photocatalysts for solar energy conversion via water splitting because it has a band gap of 2.1 eV and suitable band edge positions.^{2–5} It has been

reported that Ta₃N₅ generates hydrogen or oxygen from water under visible light in the presence of a sacrificial electron donor or acceptor, respectively.² Ta₃N₅ can also be applied as an O₂ evolution photocatalyst and as a photoanode for Z-scheme⁵ and photoelectrochemical water splitting,⁶ respectively. Comparing the two half-reactions of overall water splitting, oxygen generation is considered to be kinetically more challenging than hydrogen generation.^{7,8} It is therefore important to address this issue through the development of innovative strategies to enhance the photocatalytic activity of candidate materials for O₂ evolution. Besides cocatalyst loading to boost O₂ evolution kinetics, doping and various synthesis methods involving flux treatments have been investigated to improve the inherent physical properties of semiconductor photocatalysts.^{9–14} In general, doping has been found to have positive effects in four main areas: structural,⁹ electronic,¹⁰ optical,¹¹ and morphological.¹² Flux treatments during and after the synthesis of photocatalytic materials have been reported to alter both morphological and crystallographic aspects.^{13a}

To tailor the morphology and improve the photocatalytic performance of Ta₃N₅, a flux was utilized in the synthesis of Ta₃N₅.^{13a} It was also reported that, through doping with alkaline metal (AM) ions, the photoelectrochemical performance of nanostructured Ta₃N₅ in water oxidation could be enhanced because of tunable band gaps and an enhancement of the electrode conductivity.¹⁴ However, such positive effects are often overwhelmed by the detrimental effects of flux and dopants residues, such as decreased crystallinity and higher trap site densities, especially in photocatalytic O₂ evolution reactions where both reduction and oxidation reactions take place on the surface of Ta₃N₅ unlike photoelectrochemical reactions. In fact, reports in which the photocatalytic activity of Ta₃N₅ was actually improved by modifiers, such as a flux, or dopants are rare, indicating that innovative and controllable methods are still needed to take advantage of the favorable effects of modifiers.

We report facile modification of Ta₂O₅ with AM salts to produce a highly active Ta₃N₅ photocatalyst for water oxidation in an aqueous AgNO₃ solution under visible light irradiation. Typically, AM salts and Ta₂O₅ powder were mixed (AM/Ta = 0.1 by mole) and annealed in air at 773 K for 2 h. The AM-modified Ta₂O₅ (AM/Ta₂O₅) was then nitrided under NH₃ flow (300 mL/min) at 1123 K for 20 h, yielding AM-modified Ta₃N₅ (AM/Ta₃N₅). In some cases, the obtained AM/Ta₃N₅ was rinsed

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Table 1. Physical Properties of AM Salt-Modified Ta₃N₅

AM salt	crystallite size, nm ^a	BET surface area, m ² g ⁻¹	surface composition ^b		bulk composition ^c
			AM/Ta	N/Ta	N/(O+N)
none (Ta ₃ N ₅)	33 (32)	9.9 (10.1)	no data	0.15 (0.15)	0.96
NaCl	43 (43)	7.1 (6.3)	0.18 (0.00)	0.17 (0.17)	0.96
Na ₂ CO ₃	46 (47)	5.7 (6.0)	0.40 (0.08)	0.15 (0.14)	0.94
KCl	33 (33)	8.0 (7.6)	0.04 (0.00)	0.16 (0.12)	0.95
K ₂ CO ₃	45 (41)	5.0 (5.6)	0.10 (0.02)	0.18 (0.19)	0.94
LiCl	49 (50)	4.0 (4.5)	0.00 (0.00)	0.00 (0.00)	0.95
Li ₂ CO ₃	51 (51)	3.4 (3.9)	0.20 (0.00)	0.15 (0.14)	0.95

^aEstimated by Scherrer's equation. ^bEstimated by XPS. ^cEstimated by oxygen–nitrogen combustion analysis. Data in parentheses correspond to data obtained after washing with water.

thoroughly with water to remove AM salt residue. To obtain the highest activity, CoO_x (2 wt%) was loaded on AM/Ta₃N₅ by impregnation using a Co(NO₃)₂·6H₂O aqueous solution followed by annealing at 773 K for 1 h in an NH₃ flow^{13b} (see Supporting Information for experimental details).

All samples prepared with 10% AM salts exhibited single-phase XRD patterns associated with anosovite-type Ta₃N₅ (Figure S1A). Marginal peak shifts toward smaller diffraction angles suggested that the AM cations were not significantly incorporated into the Ta₃N₅ lattice. This is because the AM salts employed were not small enough to replace Ta⁵⁺ ions fully but rather evaporated under the nitridation conditions. Sharper diffraction peaks, larger crystallite sizes, and smaller BET surface areas (Table 1) for AM/Ta₃N₅ were indicative of higher sample crystallinity. As seen in the UV-vis diffuse reflectance spectra (DRS, Figure S1C), no noticeable change was observed in the absorption edge wavelengths among the synthesized AM/Ta₃N₅ and conventional Ta₃N₅ samples. Steep onset of light absorption at ~600 nm characteristic of Ta₃N₅ is attributable to electron transitions from N 2p orbitals to empty Ta 5d orbitals.² Since the bulk nitrogen contents were almost identical regardless of the AM salt modification, it is reasonable that the band gap energies were unchanged.

Figures 1 and S2 show changes in the surface morphology of Ta₃N₅ particles after modification with AM ions observed by

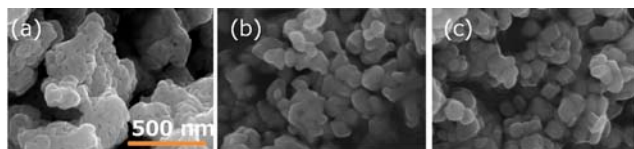


Figure 1. SEM images of Ta₃N₅ prepared from Ta₂O₅ (a) unmodified and modified with (b) NaCl and (c) Na₂CO₃.

SEM. The porous structure typical of unmodified Ta₃N₅^{13a} disappeared with the AM salt modification. All of the AM/Ta₃N₅ except Li salt/Ta₃N₅ exhibited monodisperse fine particles ~80 nm on average in size, which was considerably smaller than the particle size of the starting Ta₂O₅ and conventional Ta₃N₅ (150–400 nm). This was due to surface dissolution of the Ta₃N₅ particles and nucleation of alkali tantalate caused by the small

amount of AM salts, as discussed later. Larger particle sizes of Li salt/Ta₃N₅ were probably due to the low melting points of LiCl (886 K) and Li₂CO₃ (1005 K), and the relatively close ionic radii of the six-fold coordinated Li⁺ (90 pm) and Ta⁵⁺ (78 pm) ions, which would enable interdiffusion of the constituent cations and growth of Li salt/Ta₃N₅ particles. Note that the particle sizes estimated by SEM observation were larger than the crystallite sizes presented in Table 1 owing to possible formation of secondary particles. As shown in Table 1, the AM/Ta₃N₅ samples had lower specific surface areas than conventional Ta₃N₅. This is consistent with the lack of mesopores in the AM/Ta₃N₅ particles, as observed in SEM images. Rinsing of AM/Ta₃N₅ did not significantly change the XRD patterns, DRS, SEM images, or BET surface areas.

XPS of as-prepared Ta₃N₅ modified with NaCl, Na₂CO₃, KCl, K₂CO₃, LiCl, or Li₂CO₃ indicated the presence of the respective AM species on the surface, as shown in Table 1 and Figure S3C. After thorough washing with distilled water, signals from the AM species disappeared when chlorides were used as modifiers but not completely in the case of the carbonate modifiers. It is possible that the carbonates with higher basicity allowed for more intensive reaction with Ta₂O₅ than the chlorides, so that some of the AM species could be incorporated into the surface of the AM/Ta₃N₅. However, it is likely that the incorporation of small amounts of AM species did not strongly affect the valence states of the Ta species. Binding energies of the Ta 4f peaks were 26.6 and 28.5 eV for all of the Ta₃N₅, whether unmodified or modified with AM salts (Figure S3A). In addition, the N 1s XPS peaked at 397 eV, indicating the formation of Ta–N bonds (Figure S3B). Nitrogen contents estimated by XPS are inevitably smaller than the chemical formula because of natural oxidation layers. However, as in Table 1, surfaces of all of the prepared samples had N/Ta ratios similar to that of conventional Ta₃N₅. This suggests that the surface composition was not affected significantly by the AM salt modification. In addition, O/N combustion analysis indicated that the decrease in nitrogen-to-anion ratio (N/(N+O)) after the incorporation of AM salts was ~2% (from 96 to 94%) at most. These results confirm that Ta species predominantly existed as Ta₃N₅ and not as alkali tantalates, consistent with XRD analyses (Figure S1A) which did not indicate the presence of any crystalline impurities.

Photocatalytic O₂ evolution activity of the prepared samples before and after washing is presented in Figure 2. All of the pristine AM/Ta₃N₅ samples exhibited O₂ evolution rates more than double those of the unmodified samples. However, after rinsing with distilled water, the activity of Ta₃N₅ modified with

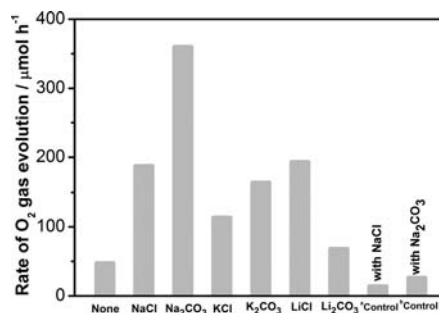


Figure 2. Rates of O₂ evolution over AM/Ta₃N₅ (AM/Ta = 0.1). Conditions: catalyst, 0.1 g; 50 mM aq AgNO₃ solution, 100 mL, 0.1 g of La₂O₃ as pH buffer; light source, 300 W xenon lamp (420 < λ < 800 nm). ^aNaCl was added and ^bNa₂CO₃ was added (Na/Ta = 0.1).

chlorides decreased markedly. It is presumably because the surface of Ta_3N_5 modified with chlorides would not be as crystalline as those modified with carbonates. As a result, they could undergo deactivation via dissolution of the surface during the rinsing. In fact, the crystallite sizes of $\text{AM}/\text{Ta}_3\text{N}_5$ prepared from $\text{NaCl}/\text{Ta}_2\text{O}_5$ and $\text{KCl}/\text{Ta}_2\text{O}_5$ were slightly smaller than those prepared from $\text{Na}_2\text{CO}_3/\text{Ta}_3\text{N}_5$ and $\text{K}_2\text{CO}_3/\text{Ta}_3\text{N}_5$ (Table 1).

Since XPS analysis indicated the presence of AM residue on the surface, one might suspect that AgCl and Ag_2O originating from chloride and carbonate residue may have contributed to the higher activity of unwashed $\text{AM}/\text{Ta}_3\text{N}_5$. However, this possibility was excluded by the control photocatalytic reactions: when an equivalent amount of sodium chloride or carbonate was intentionally added into a reaction solution containing conventional Ta_3N_5 , the O_2 evolution rates decreased. Accordingly, it is reasonable to tentatively attribute the enhanced photocatalytic activity of $\text{AM}/\text{Ta}_3\text{N}_5$ to changes in the physical properties of Ta_3N_5 , such as particle morphology, crystallinity, and donor concentrations. However, it is highly unlikely that AM ions acted as a p-type dopant because, as in Figure S4, both unmodified and Na_2CO_3 modified Ta_3N_5 photoelectrodes generated anodic photocurrents characteristic of n-type semiconductivity.^{6,14} Moreover, the onset potential of the transient anodic photocurrents under intermittent illumination did not shift positively by the Na_2CO_3 modification, suggesting that the flat band potential was not affected significantly by the marginal incorporation of Na species in Ta_3N_5 . It is reasonable to assume that the flat band potential of Ta_3N_5 is largely governed by anion vacancies rather than small amounts of AM ions, since it is widely accepted that a number of anion vacancies are generated during nitridation reaction under high-temperature ammonia flow that is highly reductive.

The effect of the AM salt modification on H_2 evolution activity was also investigated using $\text{Pt}/\text{Ta}_3\text{N}_5$ and $\text{Pt}/\text{Na}_2\text{CO}_3/\text{Ta}_3\text{N}_5$. However, the impact of AM addition on the H_2 evolution rate was not significant in preliminary trials. Since photocatalytic H_2 evolution activity depends heavily on cocatalyst loading, refinement of modification methods of Ta_3N_5 is necessary to discuss the effect of AM salt modification on the photocatalytic H_2 evolution unambiguously.

Among the AM salt precursors examined, Na_2CO_3 was found to be the most suitable for the preparation of highly active $\text{AM}/\text{Ta}_3\text{N}_5$ for O_2 evolution. Therefore, effects of O_2 evolution cocatalysts were investigated using $\text{Na}_2\text{CO}_3/\text{Ta}_3\text{N}_5$. The dependence of O_2 evolution rates on the cocatalysts loaded under various conditions is shown in Figure 3, and reaction time courses of representative samples are shown in Figure S5. Nitrogen evolution due to the oxidation of Ta_3N_5 was suppressed or not detected after cocatalyst loading (Figure S5b). $\text{Na}_2\text{CO}_3/\text{Ta}_3\text{N}_5$ samples loaded with 1 wt% Ir or 2 wt% CoO_x yielded higher O_2 evolution activity than pristine $\text{Na}_2\text{CO}_3/\text{Ta}_3\text{N}_5$, although excessive cocatalyst loading and annealing at a high temperature led to lower performance. The highest activity was obtained with 2 wt% of CoO_x loading followed by NH_3 treatment at 773 K for 1 h. Consequently, the O_2 evolution rate of conventional Ta_3N_5 increased from 55 to $450 \mu\text{mol/h}$ after modification with Na_2CO_3 and subsequent loading of the CoO_x cocatalyst, corresponding to apparent quantum efficiencies (AQYs) of 1.3 and 5.2% at 500–600 nm, respectively. The AQY of the CoO_x loaded $\text{Na}_2\text{CO}_3/\text{Ta}_3\text{N}_5$ is one of the highest values ever reported at the long wavelength region, while higher

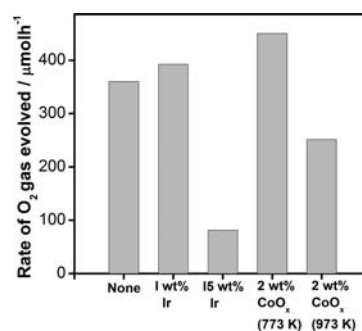


Figure 3. Rates of O_2 evolution over Na_2CO_3 -modified Ta_3N_5 loaded with Ir or CoO_x . Conditions: catalyst, 0.1 g; 50 mM aqueous AgNO_3 solution, 100 mL, 0.1 g of La_2O_3 as pH buffer; light source, 300 W xenon lamp ($420 < \lambda < 800 \text{ nm}$).

AQYs have been reported at shorter wavelengths for BiVO_4 (9% at 450 nm)¹⁵ and LaTiO_2N (27% at 440 nm).^{13b}

Importantly, effects of AM salt modification and the catalytic enhancement by CoO_x loading were accumulative. Considering the structural features, photocatalytic activity, and photoelectrochemical properties together, it is reasonable to attribute the positive effects of AM salt modification on photocatalytic O_2 evolution to smaller particle sizes ($\sim 80 \text{ nm}$ on average) and/or improved crystallinity of the resultant Ta_3N_5 . Smaller particle sizes allow photoexcited carriers to migrate to surface active sites more readily, and improved crystallinity provides fewer trap sites and thereby more photoexcited carriers for surface reactions. It is thus of interest to clarify how AM salts (Na_2CO_3 in particular) alter the morphology and crystallinity of the resulting Ta_3N_5 .

Figures 4 and S6(i) show SEM images and XRD patterns of samples at different stages of the nitridation of $\text{Na}_2\text{CO}_3/\text{Ta}_2\text{O}_5$

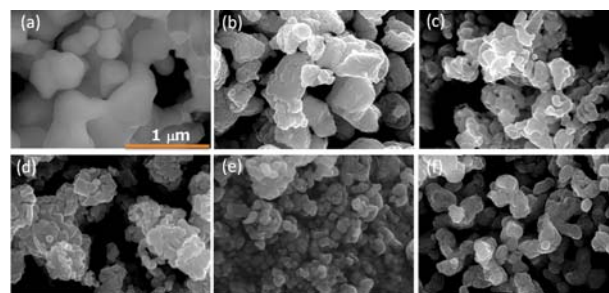


Figure 4. SEM images of $\text{Na}_2\text{CO}_3/\text{Ta}_2\text{O}_5$ (a) before and after nitridation for (b) 1, (c) 5, (d) 10, and (e) 20 h; (f) corresponds to unmodified Ta_2O_5 nitrided for 20 h.

into $\text{Na}_2\text{CO}_3/\text{Ta}_3\text{N}_5$, respectively. The intermediate TaON phase was formed in 1 h of nitridation. Even at this initial stage, the particles began to be miniaturized and exhibit well-defined shapes, although large agglomerated clusters still remained. In contrast, the sample without Na_2CO_3 modification did not show any significant reduction in particle size (Figure S7). After 5 h of nitridation, the Na_2CO_3 -modified sample exhibited more dispersed particles, which were $\sim 100 \text{ nm}$ in size, and the sample showed no sign of the porosity characteristic of TaON and Ta_3N_5 . Further nitridation of this sample resulted in complete conversion to Ta_3N_5 and somewhat smaller particles ($\sim 80 \text{ nm}$ on average) as a result of the substitution of two N^{3-} ions for three O^{2-} ions and sintering. It is noteworthy that NaTaO_3 was formed in addition to TaON at the early stage of the nitridation while not being observed in the final product. This suggests that

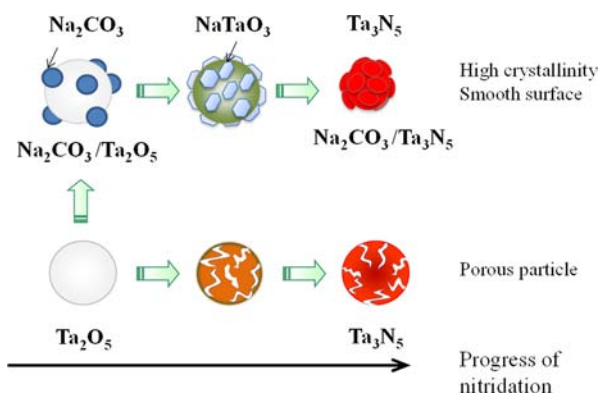


Figure 5. Proposed scheme for evolution of conventional Ta_3N_5 (bottom) and $\text{Na}_2\text{CO}_3/\text{Ta}_3\text{N}_5$ (top).

Na_2CO_3 reacted with Ta_2O_5 to form NaTaO_3 under the present nitridation conditions, and the nucleation of NaTaO_3 could be responsible for the surface reorganization of $\text{Na}_2\text{CO}_3/\text{Ta}_2\text{O}_5$ particles upon nitridation. Prolonged nitridation resulted in production of Ta_3N_5 without secondary phases because of volatilization of Na species. Transient formation of KTaO_3 during nitridation of $\text{K}_2\text{CO}_3/\text{Ta}_2\text{O}_5$ was also confirmed (Figure S6(ii)), attesting the above-mentioned nitridation process. Note that XRD patterns of $\text{Na}_2\text{CO}_3/\text{Ta}_3\text{N}_5$ with different amounts of Na_2CO_3 revealed the presence of NaTaO_3 at initial Na/Ta ratios higher than 0.2 even after 20 h of nitridation (Figure S8). Evolution of NaTaO_3 was also previously observed when excessive Na_2CO_3 or NaCl was added to Ta_2O_5 during nitridation.^{13a} The use of the small amount of Na_2CO_3 was thus essential to prevent formation of residual byproducts while allowing for nucleation of NaTaO_3 on the surface.

Based on the above results, a proposed development scheme of highly active $\text{Na}_2\text{CO}_3/\text{Ta}_3\text{N}_5$ photocatalysts can be summarized as illustrated in Figure 5 and the corresponding SEM images (Figure S7). The addition of Na_2CO_3 provided dispersed particles of smaller sizes and improved the crystallinity as a result of the nucleation of NaTaO_3 in the initial stages of nitridation. Further nitridation led to evaporation of Na species and sintering of the ansovite-type Ta_3N_5 . Some residue could have remained on the surface, without contributing to the activity enhancement. Furthermore, the very small amounts of Na_2CO_3 used would not significantly change the semiconducting properties of Ta_3N_5 , such as the band gap energy or the flat band potential by acting as dopants, since the amount of Na-species were considerably low.

In summary, the surface loading of AM salts onto Ta_2O_5 (AM/Ta = 0.1 in molar ratio) was found to be a facile and effective method to improve the water oxidation activity of Ta_3N_5 . In particular, $\text{Na}_2\text{CO}_3/\text{Ta}_3\text{N}_5$ exhibited smaller particles with better crystallinity because of partial dissolution of Ta_2O_5 and nucleation of NaTaO_3 grains. The smaller particle sizes and improved crystallinity are thought to be the principal reasons for the activity enhancement. The present work demonstrates that even a surface modification, such as AM salt loading onto a starting material, can greatly improve the quality and performance of photocatalytic materials, offering a breakthrough in the development of photocatalysts for solar water splitting. Further investigations are in progress to understand the roles of AM salts and relationship between the physicochemical properties and photocatalytic activity.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details and characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

domen@chemsys.t.u-tokyo.ac.jp

Present Address

[‡]Department of Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology, Japan

Notes

The authors declare no competing financial interest.

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