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Modified Ta_3N_5 Powder as a Photocatalyst for O_2 Evolution in a Two-Step Water Splitting System with an Iodate/Iodide Shuttle Redox Mediator under Visible Light

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Modification of tantalum nitride (Ta_3N_5), which has a band gap of 2.1 eV, with nanoparticulate iridium (Ir) and rutile titania (R-TiO_2) achieved functionality as an O_2 evolution photocatalyst in a two-step water-splitting system with an IO_3^-/I^- shuttle redox mediator under visible light ($\lambda > 420$ nm) in combination with a Pt/ZrO_2/TaON H_2 evolution photocatalyst. The loaded Ir nanoparticles acted as active sites to reduce IO_3^- to I^-, while the R-TiO_2 modifier suppressed the adsorption of I^- on Ta_3N_5, allowing Ta_3N_5 to evolve O_2 in the two-step water-splitting system.

Photocatalytic water splitting into H_2 and O_2 by semiconducting catalysts has received much attention due to the potential for the production of clean H_2 fuel from water using solar energy.[1] Although many photocatalysts that function efficiently under ultraviolet (UV) irradiation have been developed, only a few visible light responsive photocatalysts, such as $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$,[2] have been reported for overall water splitting. The absorption edge for these photocatalysts is around 500 nm.[1b] To efficiently utilize solar energy, however, compounds with absorption bands at even longer wavelengths are required. There have been some reports that (oxy)nitrides of early transition metals with d^0-electronic configurations (e.g., Ta^{5+}, Nb^{5+}, and Ti^{4+}) are potential candidates for visible light induced water splitting.[1b] The valence bands of these materials are populated by N2p (mixed with O2p) electrons, resulting in less positive valence band levels and smaller band gaps, compared to oxide semiconductors. For example, tantalum nitride (Ta_3N_5) with a band gap of 2.1 eV (absorption edge at 600 nm) has conduction and valence band edges at ca. -0.4 and $+1.7$ V vs NHE, respectively, at pH 0. Ta_3N_5 also has a high quantum efficiency (QE) of up to 10% for water oxidation to O_2 under visible light with Ag^+ as a sacrificial electron acceptor.[3,4] However, overall water splitting has not yet been achieved with a d^0-type (oxy)nitride photocatalyst.

On the other hand, successful two-step water-splitting systems, called Z-schemes, in which two different photocatalysts are combined using a proper shuttle redox mediator, have been reported for several combinations of photocatalysts and redox shuttles.[5−14] In these systems, a wider range of visible light can be utilized than in conventional water-splitting systems because the energy required to drive each photocatalyst is reduced. Very recently, Z-scheme systems that do not rely on any redox mediator have been reported.[15,16] The authors have reported such a system using oxynitrides.[11−14] The absorption wavelength available for H_2 evolution was increased to 660 nm using $BaTaO_2N$,[13] but the limit for O_2 evolution remained 500 nm (TaON).[12] The replacement of TaON by a photocatalyst with a longer absorption edge would enable more efficient utilization of visible light. Therefore, Ta_3N_5 is a promising candidate as an O_2 evolution photocatalyst for a Z-scheme water-splitting system, because it absorbs light up to 600 nm and evolves O_2 with a relatively high QE, as mentioned above. However, photocatalytic water oxidation to O_2 can be difficult to achieve because the reaction involves a four-electron process, which is especially challenging when a reversible electron acceptor (e.g., IO_3^-) and a narrow-gap photocatalyst (Ta_3N_5) are used.

In this work, modified Ta_3N_5 was prepared as a photocatalyst for O_2 evolution in a Z-scheme water-splitting system using an IO_3^-/I^- redox mediator. Ta_3N_5 loaded with iridium (Ir) was active for O_2 evolution in the presence of IO_3^- as an electron

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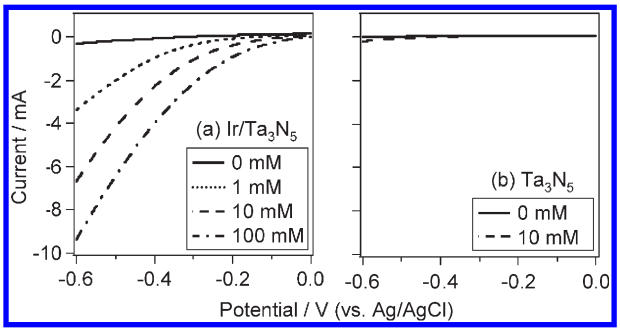

Figure 1. $I-V$ characteristics of Ta_3N_5 electrodes (a) with and (b) without loading Ir in aqueous solution containing different concentrations of $NaIO_3$.

acceptor. Additionally, loading rutile titania (R-TiO_2) effectively controlled the surface adsorption of the IO_3^-/I^- redox pair, suppressing the backward reaction. By combining the above with TaON loaded with nanoparticulate ZrO_2 and Pt (Pt/ZrO_2/TaON)[14] as an H_2 evolution photocatalyst, a Z-scheme type system for overall water splitting under visible light ($\lambda > 420$ nm) was achieved.

First, we examined photocatalytic O_2 evolution over Ta_3N_5 loaded with various cocatalysts in the presence of IO_3^- as an electron acceptor under visible light (Table S1, Supporting Information). The following elementary reactions occur on a photocatalyst during O_2 evolution from an aqueous $NaIO_3$ solution under visible light:[9]

$$\text{photocatalyst} + h\nu\ (> \text{band gap energy}) \rightarrow e^- + h^+ \qquad (1)$$

$$2H_2O + 4h^+ \rightarrow O_2 + 4H^+\ (\text{valence band}) \qquad (2)$$

$$IO_3^- + 6e^- + 3H_2O \rightarrow I^- + 6OH^-\ (\text{conduction band}) \qquad (3)$$

Although bare Ta_3N_5 had no O_2-evolution activity, Ru/Ta_3N_5, Rh/Ta_3N_5, and Ir/Ta_3N_5 evolved O_2 from an aqueous solution containing IO_3^-, and Ir/Ta_3N_5 exhibited the highest O_2 evolution activity (34.0 μmol h^{-1}). The production of I^- anions in the solution after O_2 evolution over Ir/Ta_3N_5 was confirmed qualitatively by ion chromatography, although an accurate quantitative determination of the I^- concentration was difficult due to the adsorption of I^- onto the photocatalyst powder. These results suggested the possibility that Ir/Ta_3N_5 could be applied as a building block for O_2 evolution in a Z-scheme with an IO_3^-/I^- shuttle redox mediator.

X-ray photoelectron spectroscopy indicated that the valence state of the loaded Ir was identical to that of metallic Ir powder (Figure S1, Supporting Information). It was also revealed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) that Ir nanoparticles about 5 nm in size were loaded on the Ta_3N_5 (Figure S2, Supporting Information). To clarify the function of the Ir cocatalyst, electrochemical measurements were conducted using porous Ta_3N_5 electrodes in an aqueous solution containing IO_3^- ions. These measurements indicated that the reduction of IO_3^- on the surface of Ta_3N_5 is difficult, as little current was observed in the unmodified Ta_3N_5 electrode (Figure 1b). However, an appreciable cathodic current was observed in an Ir-modified Ta_3N_5 electrode, and this current was markedly increased by the addition of IO_3^- ions to the solution (Figure 1a). The Ir cocatalyst loaded on Ta_3N_5 greatly assisted the reduction of IO_3^-, probably by functioning as an active site for that reduction. Moreover, while bare Ta_3N_5 photocatalyst resulted in no H_2 evolution activity from an aqueous solution containing methanol as an electron donor, Ir/Ta_3N_5 photocatalyst exhibited H_2 evolution activity in the presence of methanol. These results further support the idea that Ir on Ta_3N_5 functions as a cocatalyst promoting the reduction reaction. In summary, efficient O_2 evolution from an aqueous solution containing IO_3^- proceeds over Ir/Ta_3N_5 because the metallic Ir nanoparticles function as active sites for the reduction of IO_3^-. However, it is noted that the metallic state of Ir cocatalysts on Ta_3N_5 was not completely stable during reaction, undergoing oxidation to IrO_x to some extent. XPS analysis showed that the Ir 4f photoelectron signal assigned to Ir metal remained largely unchanged, but shoulder peak(s) at higher binding energy side got enlarged after O_2 evolution reaction (Figure S1, Supporting Information).

Table 1. Initial Rate of O_2 Evolution on Modified Ta_3N_5 Photocatalysts from Aqueous $NaIO_3$ Solution (4 mM) under Visible Light ($\lambda >$ 420 nm)[a]

		rate of O_2 evolution (μmol·h^{-1})	
entry	catalyst	without NaI additive	with NaI additive (1 mM)
1	Ta_3N_5	0	0
2	Ir/Ta_3N_5	25.0	0.8
3	Ir/R-TiO_2/Ta_3N_5	19.8	8.2
4	Ir/R-TiO_2	0	0
5	R-TiO_2/Ta_3N_5	0	0
6	Ir/A-TiO_2/Ta_3N_5	24.1	1.8

[a] Reaction conditions: catalyst, 0.05 g (Ir 5 wt % loaded); aqueous solution, 250 mL; light source, xenon lamp (300 W) fitted with a cutoff filter; reaction vessel, Pyrex side-irradiation type.

Table 1 shows the O_2 evolution activity of the modified Ta_3N_5 photocatalysts in aqueous $NaIO_3$ solution with and without the intentional addition of NaI. Although Ir/Ta_3N_5 evolved O_2 in the presence of IO_3^-, the activity decreased significantly when even a small amount of I^- was added to the solution (entry 2). This can be attributed to the backward reaction (oxidation of I^-) that can occur in the valence band of an O_2 evolution photocatalyst:[9]

$$I^- + 6h^+ + 6OH^- \rightarrow IO_3^- + 3H_2O\ (\text{valence band}) \qquad (4)$$

Since the redox potentials of O_2/H_2O and IO_3^-/I^- are 1.23 and 1.09 V (vs NHE at pH 0), respectively, the oxidation of I^- to IO_3^- is thermodynamically favorable compared with that of H_2O to O_2. As a result, in an aqueous solution containing both IO_3^- and I^-, the preferential oxidation of I^- to IO_3^- occurs, instead of H_2O oxidation on the Ir/Ta_3N_5 photocatalyst.

The suppression of this backward reaction is necessary to apply Ta_3N_5 to an O_2 evolution system in the Z-scheme, because both I^- and IO_3^- ions exist in the Z-scheme overall water-splitting environment. Rutile titania (R-TiO_2) has been reported as a photocatalyst for O_2 evolution with a unique surface adsorption property:[9] IO_3^- ions adsorb more easily than I^- ions onto the surface of R-TiO_2. This property allows R-TiO_2 to selectively promote O_2 evolution using IO_3^- as an electron acceptor, even in the presence of a considerable amount of I^- in the solution. We thus attempted to support R-TiO_2 on Ta_3N_5 according to the method by Gopal et al.[17] SEM and TEM observation of this R-TiO_2/Ta_3N_5 showed that the Ta_3N_5 surface was covered with nanoparticulate R-TiO_2 (Figure 2b,c). It should be noted that the particle size of Ta_3N_5 (200−500 nm) remains unchanged upon

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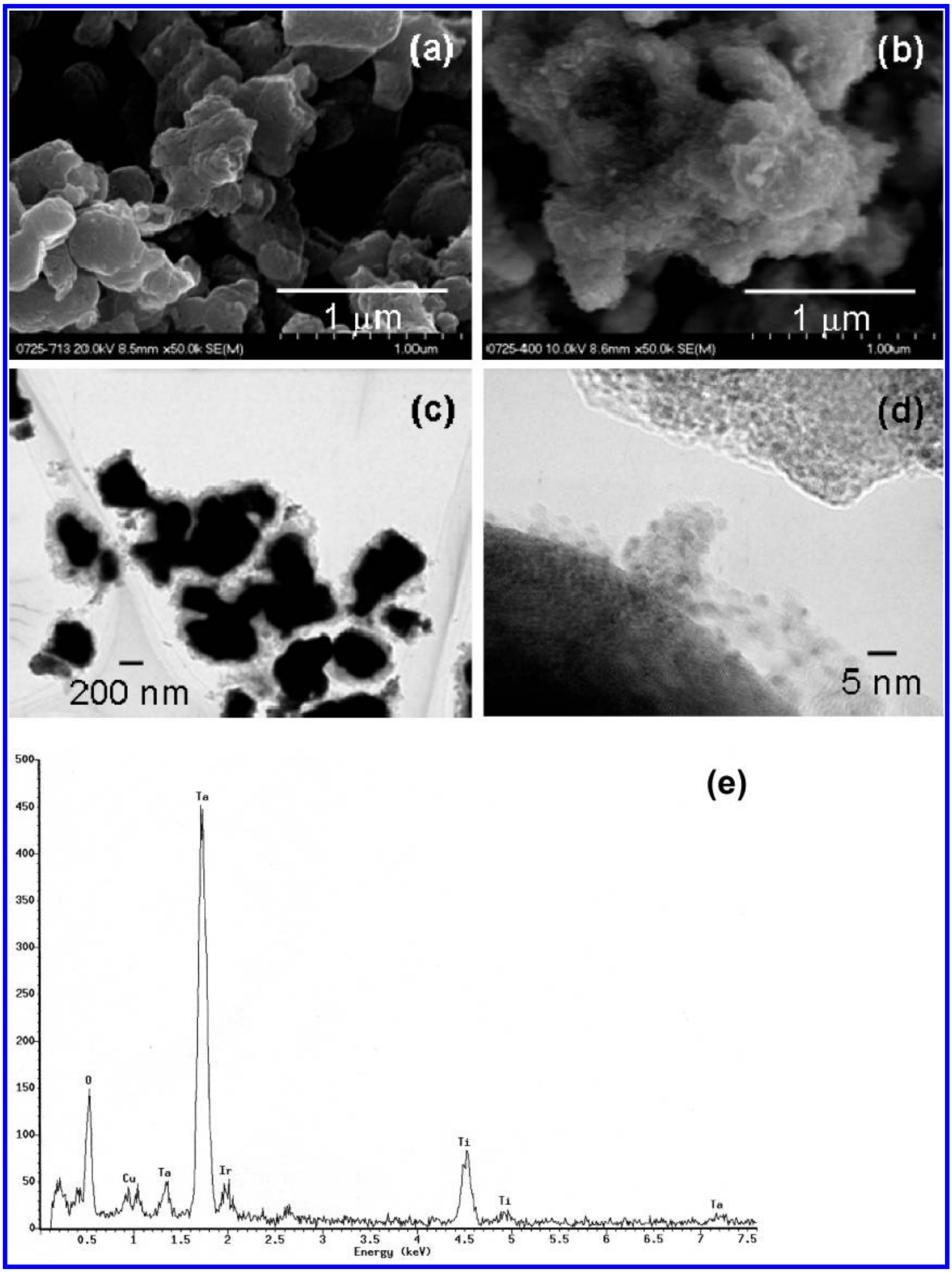

Figure 2. SEM images of (a) Ta_3N_5 and (b) R-TiO_2/Ta_3N_5 and TEM images of (c) R-TiO_2/Ta_3N_5 and (d) Ir/R-TiO_2/Ta_3N_5. Panel (e) indicates the EDX spectrum of the sample shown in (d).

modification with R-TiO_2 (Figure 2a,c). Although there was little difference between the X-ray diffraction (XRD) patterns of Ta_3N_5 and R-TiO_2/Ta_3N_5, the preparation of R-TiO_2 by the method reported in the literature, without Ta_3N_5, resulted in the production of TiO_2 with a rutile structure (Figure S3, Supporting Information). Therefore, nanoparticulate rutile TiO_2 was successfully introduced onto the Ta_3N_5 surface, although its detection by XRD was difficult, due primarily to the small particle size.

As shown in Table 1, the O_2 evolution activity of Ir/R-TiO_2/Ta_3N_5 in an aqueous solution containing both IO_3^- and I^- (entry 3) was 10 times higher than that of Ir/Ta_3N_5 (entry 2). In this enhancement, R-TiO_2 functioned not as a photocatalyst but as a modifier, because Ir-loaded R-TiO_2 prepared as in the literature, without Ta_3N_5, did not evolve O_2 from an aqueous solution containing IO_3^- under visible light irradiation (entry 4). In addition, R-TiO_2/Ta_3N_5 without Ir cocatalyst showed no O_2 evolution activity in aqueous $NaIO_3$ solution (entry 5), indicating that the R-TiO_2 prepared in this study did not function as a cocatalyst to promote the surface reaction. It was difficult to estimate the difference in the amount of adsorbed ions between Ir/Ta_3N_5 and Ir/R-TiO_2/Ta_3N_5 because of their small amounts. However, since Ir/R-TiO_2/Ta_3N_5 should selectively adsorb IO_3^- and hinder the access of I^-, as does R-TiO_2 alone, this effect should enhance the O_2 evolution from Ir/R-TiO_2/Ta_3N_5 in an aqueous solution containing both IO_3^- and I^-. More specifically, it is likely that O_2 evolution occurs at the boundary region among R-TiO_2, Ta_3N_5, and the reactant solution. In this region, adsorption of I^- anions onto Ta_3N_5 (in other words, scavenging photogenerated holes by the adsorbed I^- anions) becomes weaker, thereby allowing for O_2 evolution. Interestingly, a similarly prepared sample, TiO_2-anatase modified Ta_3N_5 (A-TiO_2/Ta_3N_5), did not work as effectively as R-TiO_2/Ta_3N_5 (entry 6). According to the previous report, A-TiO_2 does not have the aforementioned unique adsorption property observed in R-TiO_2.[9] This result further supports the idea that the relatively high activity of Ir/R-TiO_2/Ta_3N_5 is attributed to the R-TiO_2 modifier on Ta_3N_5, which hinders the access of I^- anions.

TEM observation of Ir/R-TiO_2/Ta_3N_5 showed that the Ir particles (i.e., reduction sites) were loaded mainly on the R-TiO_2 component (Figure 2d). The existence of Ir and R-TiO_2 on Ta_3N_5 was also confirmed by energy dispersive X-ray (EDX) analysis (Figure 2e). To verify the function of the Ir particles on R-TiO_2, we examined photocatalytic O_2 evolution on R-TiO_2 (purchased from Kanto Chemical Co., Inc.) loaded with and without Ir in a solution containing IO_3^- under UV irradiation ($\lambda > 300$ nm). The initial rate of O_2 evolution on Ir/R-TiO_2 was about three times that of R-TiO_2 alone. This indicates that Ir particles loaded on R-TiO_2 also function as active sites for the reduction of IO_3^-, similar to the Ir particles on Ta_3N_5 described above. From these results, we conclude that the pathway of electrons and holes is as follows. When Ir/R-TiO_2/Ta_3N_5 is irradiated by visible light, electrons and holes are generated in the conduction and valence bands of Ta_3N_5, respectively. The electrons are injected into R-TiO_2, driven by the difference in their conduction band edge positions (Ta_3N_5: −0.4 V, R-TiO_2: 0 V vs NHE at pH 0), and reduce IO_3^- at Ir particles on the R-TiO_2. On the other hand, the holes oxidize water to produce O_2 on the surface of Ta_3N_5. The recombination of electrons and holes in the Ta_3N_5 is suppressed by electron transfer from Ta_3N_5 to R-TiO_2, leading to the enhanced activity of Ir/R-TiO_2/Ta_3N_5 shown in Table 1.

Finally, visible-light-driven overall water splitting was attempted by combining Pt/ZrO_2/TaON as an H_2 evolution photocatalyst with the newly developed Ir/R-TiO_2/Ta_3N_5 as an O_2-evolution photocatalyst in an aqueous NaI solution.[18] As shown in Figure 3, simultaneous evolution of H_2 and O_2 was observed. At the initial stage of the reaction, IO_3^- was accumulated as a result of the oxidation of I^- on Pt/ZrO_2/TaON, and O_2 evolution began to occur on Ir/R-TiO_2/Ta_3N_5. As the reaction proceeded, the accumulated IO_3^- suppressed H_2 evolution by Pt/ZrO_2/TaON. At the steady state, the rates of H_2 and O_2 evolution became relatively stable, although the H_2/O_2 ratio in the products was slightly larger than that expected from the stoichiometry ($H_2/O_2 = 2$). Empirically, such nonstoichiometric H_2 and O_2 evolution in Z-scheme water splitting using an IO_3^-/I^- redox pair tends to be observed when competitive oxidation of I^- on an O_2 evolution photocatalyst is significant (i.e., the reactivity of the valence band holes in the O_2 evolution photocatalyst with I^- is high and/or the concentration of NaI is high).[9,14b] Control experiments showed no simultaneous evolution of H_2 and O_2 when any one component of the system (Pt/ZrO_2/TaON, Ir/R-TiO_2/Ta_3N_5, NaI, and the light source) was absent. In addition, the total production of H_2 and O_2 after 60 h was ca. 200 μmol, substantially larger than the amount of NaI employed as a shuttle redox mediator (25 μmol) for the reaction. These results clearly indicate that the overall water splitting proceeded photocatalytically by a redox cycle between IO_3^- and I^- as follows: (I) water reduction to H_2 and I^- oxidation to IO_3^- over Pt/ZrO_2/TaON and (II) IO_3^- reduction to I^- and water oxidation to O_2 over Ir/R-TiO_2/Ta_3N_5. It is known that iodine species (e.g., iodide, iodate, and triiodide) undergo chemical changes such as comproportionation and disproportionation. However, we did not observe them in the present system, due primarily to the relatively low optimal NaI concentration (0.1 mM) and the low reactivity of this system. Although we confirmed the reproducibility of the simultaneous H_2 and O_2 evolution in the case of Ir/R-TiO_2/Ta_3N_5 as an O_2 evolution photocatalyst, the reproducibility of O_2 evolution was poor when Ir/Ta_3N_5 (without R-TiO_2) was used. Furthermore, unmodified Ta_3N_5 did not function as an O_2 evolution photocatalyst in the above-mentioned Z-scheme water-splitting system. Therefore, modification of the Ta_3N_5 surface with both Ir cocatalyst and R-TiO_2 nanoparticles was required to achieve Z-scheme overall water splitting. We expect that the overall efficiency of this catalytic system will be improved by further refinement of the catalyst preparation, and this possibility is currently under investigation.

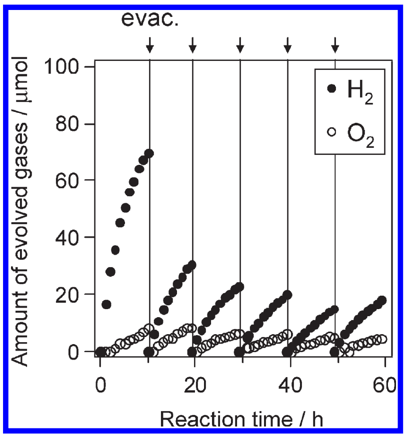

Figure 3. Time course of photocatalytic evolution of H_2 and O_2 using a mixture of Pt/ZrO_2/TaON and Ir/R-TiO_2/Ta_3N_5 suspended in aqueous NaI solution under visible light ($\lambda > 420$ nm). Reaction conditions: catalyst, 0.05 g each; aqueous NaI solution, 250 mL (0.1 mM); light source, xenon lamp (300 W) fitted with a cold mirror (CM-1) and a cutoff filter; reaction vessel, Pyrex side-irradiation type. Pt (1 wt %) and Ir (5 wt %) were deposited on ZrO_2/TaON and R-TiO_2/Ta_3N_5, respectively, by impregnation.

It is also noted that the rates of H_2 and O_2 evolution decreased slightly with time, but recovered after evacuation of the reaction system, suggesting that H_2-O_2 recombination, which is thermodynamically favorable, takes place during the reaction. This was confirmed by testing the water formation reaction from a mixture of H_2 and O_2 in the dark using Pt/ZrO_2/TaON and Ir/R-TiO_2/Ta_3N_5 catalysts. As shown in Figure S5 (Supporting Information), the amounts of H_2 and O_2 in a closed-gas circulation system both decreased with time, indicating that water formation (eq 5 below) occurs on a mixture of Pt/ZrO_2/TaON and Ir/R-TiO_2/Ta_3N_5.

$$2H_2 + O_2 \rightarrow 2H_2O \qquad (5)$$

It is thus clear that, during photocatalytic water splitting, this undesirable reaction occurs, thereby reducing the detected rates of H_2 and O_2 evolution. The suppression of the H_2-O_2 recombination is another important subject to realize more efficient water splitting in this reaction system.

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(18) UV−visible diffuse reflectance spectra of ZrO_2/TaON and R-TiO_2/Ta_3N_5 are included in the Supporting Information (Figure S4). More detailed results of the characterization of ZrO_2/TaON modified with or without Pt have been reported elsewhere (see ref 14).

In conclusion, Ta_3N_5 with a band gap of 2.1 eV was successfully applied as an O_2 evolution photocatalyst in a two-step water-splitting system with an IO_3^-/I^- shuttle redox mediator under visible light ($\lambda > 420$ nm). This was accomplished after proper modification to offer catalytic active sites for the reduction of IO_3^- ions and hinder undesirable I^- adsorption. Previous research on water splitting photocatalysts has been directed mainly toward the development of photocatalysts which minimize electron–hole recombination and maximize absorption capability.[1] As a result, surface modification of photocatalysts to improve their selectivity for two-step water splitting has been neglected. The present result thus expands the possibility of using various photocatalysts (including (oxy)nitrides) in two-step water-splitting systems, by employing a suitable modification method to construct reaction sites and control the adsorption of redox reagents.

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Supporting Information Available: Experimental details, table of photocatalytic activities on Ta_3N_5 loaded with various cocatalysts, XPS spectra for Ir 4f, SEM and TEM images of Ir/Ta_3N_5, XRD pattern for R-TiO_2/Ta_3N_5, UV–visible diffuse reflectance spectra for ZrO_2/TaON and R-TiO_2/Ta_3N_5, and time course of water formation in the dark over Pt/ZrO_2/TaON and Ir/R-TiO_2/Ta_3N_5 suspended in an aqueous NaI solution. This material is available free of charge via the Internet at http://pubs.acs.org.