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COMMUNICATION

Na-containing Pt cocatalyst for efficient visible-light-induced hydrogen evolution on BaTaO₂N

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A high degree of cocatalyst dispersion and intimate contact with the photocatalyst are vital for improving the activity of narrow bandgap photocatalytic materials. In this work, the addition of small amounts of Na ions to a Pt cocatalyst deposited on a semiconducting BaTaO₂N photocatalyst (with an absorption edge of 650 nm) enhanced photocatalytic H₂ evolution under visible light irradiation. The addition of Na ions to the Pt-loaded BaTaO₂N (Pt/BaTaO₂N) caused more efficient evolution of H₂ than Na-free Pt/BaTaO₂N during Z-scheme overall water splitting. These results should assist in the fabrication of photocatalysts modified with highly dispersed cocatalysts for efficient water splitting.

Water splitting using particulate semiconductor photocatalysts has attracted attention as a means of producing renewable solar hydrogen. BaTaO₂N, which has an absorption edge wavelength of 650 nm, is a promising photocatalyst for this purpose, because it is able to utilize a wide range of the solar spectrum.¹ Noble metals such as Pt are also widely used as cocatalysts to promote the H₂ evolution reaction on the surface of BaTaO₂N,²⁻⁴ by improving charge separation and transport across the photocatalyst junction, and also serving as active sites.⁵ Accordingly, both the particle size and dispersion of the cocatalyst significantly affect the photocatalytic activity.⁶⁻⁷ In earlier studies, Pt-loaded BaTaO₂N (Pt/BaTaO₂N) was obtained by impregnation with Pt followed by reduction under H₂. This

material was found to be more active during the H₂ evolution reaction from an aqueous methanol solution compared with a catalyst fabricated using photodeposition, as a result of stronger interactions between the photocatalyst and the cocatalyst particles.⁸⁻¹⁰ However, the tendency of Pt nanoparticles to aggregate can lead to reduced performance, and so must be addressed.

The addition of species incorporating alkali metals is known to improve the activity of Pt-based thermal- and electrocatalysts supported on a variety of oxides, including ZrO₂, CeO₂, TiO₂ and Al₂O₃.¹¹⁻¹³ A prior study of electrocatalytic fuel-cell reactions on Pt found that adding alkali metal cations (M⁺(H₂O)_x) promoted the formation of adsorbed OH (OH_{ad}) on the Pt while suppressing that of oxygen-containing species such as O₂⁻ and H₂O₂, even though the alkali metal cations themselves were not directly adsorbed on the Pt.¹⁴ These results suggested that interactions occur between the Pt surface and hydrated alkali metal cations adsorbed in the vicinity of the surface.¹⁴ Additional work determined that each metal cation is in close contact and undergoes noncovalent interactions with two adjacent OH_{ad} groups, which stabilizes the adsorption of these groups.¹⁴ These interactions in the immediate vicinity of the Pt surface can affect the surface charge density and hence also improve the stability of Pt cocatalysts.¹¹⁻¹⁴ It has also been suggested that small metallic Pt nanoparticles promote both electron transfer and H-H coupling.¹⁵⁻¹⁸

Prior studies have indicated that the addition of alkali cations can significantly affect the dispersion and chemical state of the Pt cocatalyst, and thus can enhance the H₂ evolution activity of a Pt/BaTaO₂N photocatalyst. Herein, we demonstrate that the addition of Na ions to a Pt/BaTaO₂N photocatalyst during the impregnation process, with subsequent H₂ reduction, produces stable, well-dispersed Pt nanoparticles. As a result of this modification, the photocatalytic activity of this material is more than doubled during both H₂ evolution from an aqueous methanol solution and Z-scheme overall water splitting.

In the present work, BaTaO₂N powder having an absorption edge of 650 nm was synthesized via thermal nitridation in a RbCl

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flux (Fig. S1).⁸ After thermal nitridation and subsequent washing and drying, perovskite-type BaTaO₂N was obtained as the major product, but a small amount of Ta₃N₅ was also generated. This impurity phase was unfavorable for hydrogen evolution over BaTaO₂N. Our previous work suggested that the formation of Ta₃N₅ impurity phase was suppressed by controlling the contents of BaCO₃ and RbCl in the starting materials.⁸ A Pt cocatalyst was subsequently loaded using an impregnation process, either with or without Na, followed by H₂ reduction at 523 K for 1 h (unless otherwise noted). Fig. 1(a) plots the extent of H₂ evolution over 0.28 wt% Pt/BaTaO₂N samples with and without the addition of 0.23 wt% Na, in aqueous methanol. The Na-containing and Na-free Pt/BaTaO₂N evolved 255 and 90 μmol of H₂ in 1 h, respectively, confirming the beneficial effect of incorporating Na on photocatalytic H₂ evolution. The H₂ evolution reaction was subsequently performed using 0.28 wt% Pt/BaTaO₂N photocatalyst samples made with varying amounts of Na. As shown in Fig. 1(b), with increasing Na addition, the H₂ evolution rate increased abruptly and then decreased rapidly. The optimum level of Na addition was evidently 0.23 wt%, corresponding to a Na/Pt molar ratio of 7. As shown in Fig. S2 and S3, the highest degree of H₂ evolution activity was obtained with 0.28 wt% Pt and 0.23 wt% Na, employing a reduction temperature of 523 K. The apparent quantum yield for the H₂ evolution reaction was approximately 1% at 420 nm. This is superior to most BaTaO₂N-related photocatalysts but inferior to the latest Pt-loaded BaTaO₂N, where Pt was loaded by impregnation-reduction and photodeposition stepwise, recently reported from our group.¹⁹

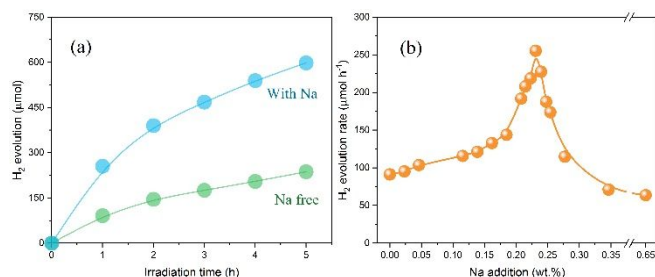


Fig. 1. a) Time courses of H₂ evolution over 0.28 wt% Pt/BaTaO₂N with and without 0.23 wt% Na. b) H₂ evolution rates over Na-containing 0.28 wt% Pt/BaTaO₂N as a function of Na addition. Reaction conditions: 100 mg of photocatalyst; 150 mL aqueous methanol solution (15 vol.%); light source, Xe lamp (420 nm < λ < 800 nm).

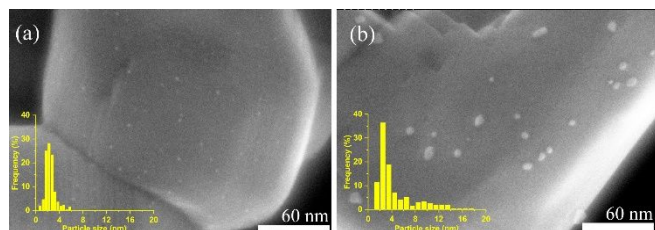


Fig. 2. STEM images and particle size distributions (insets, 300 particles counted) obtained for (a) 0.23 wt% Na-containing and (b) Na-free 0.28 wt% Pt/BaTaO₂N samples after hydrogen reduction at 523 K for 1 h.

The content of Na in the Na-containing Pt/BaTaO₂N was largely consistent to that introduced in the impregnation process as shown in Table S1. However, only a small amount of Na was detected after the 5-h reaction. Moreover, loading of NaOH prior to the loading of the Pt cocatalyst did not enhance the H₂ evolution activity of the BaTaO₂N photocatalyst (Fig. S4). These results indicate that Na was not doped in the lattice of BaTaO₂N and was dissolved in the reaction solution during the reaction. Therefore, the enhanced photocatalytic activity using the Na-containing Pt cocatalyst should be ascribed to changes in the Pt cocatalyst.

The structure of the 0.23 wt% Na-containing 0.28 wt% Pt/BaTaO₂N photocatalyst, which was the most active, was compared with that of the Na-free analogue by obtaining scanning transmission electron microscopy (STEM) images and particle size distributions (Fig. 2). The Pt nanoparticles on the former material were both smaller and better dispersed (Fig. 2(a)) compared with the latter sample (Fig. 2(b)). Specifically, the addition of Na ions during the impregnation process resulted in more than 94% of the Pt particles having sizes smaller than 4 nm, and no large Pt particles (> 6 nm) were observed. In contrast, the Na-free specimen had some small nanoparticles but more than 15% of the Pt particles exceeded 8 nm.

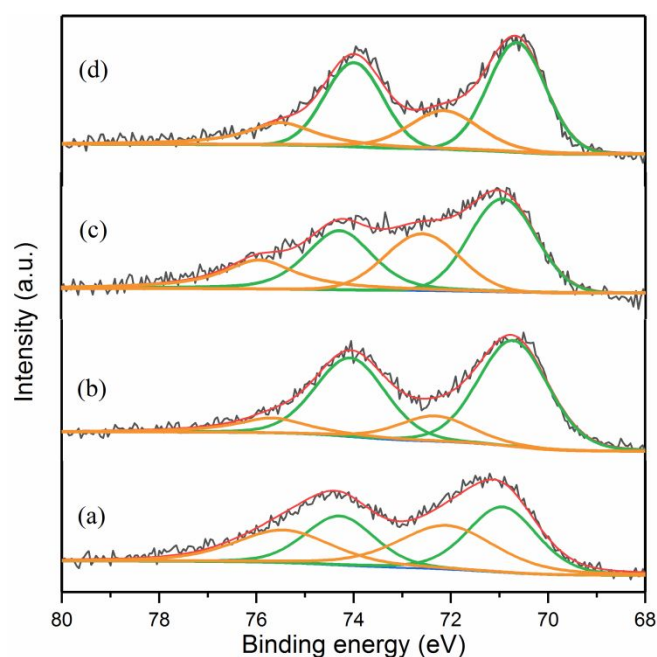


Fig. 3. Pt 4f XPS spectra of (a,b) Na-containing and (c,d) Na-free Pt/BaTaO₂N (a,c) before and (b,d) after 5 h H₂ evolution reactions.

X-ray photoelectron spectroscopy (XPS) was used to examine the effects of Na addition on the chemical state of the Pt cocatalyst on BaTaO₂N, as shown in Fig. 3. The Pt 4f_{7/2} peak generated by the Na-containing Pt/BaTaO₂N at 70.9 eV is ascribed to metallic Pt⁰, while that at 72.1 eV can possibly be attributed to partially oxidized Pt species.¹¹⁻¹³ The Na-free Pt/BaTaO₂N also produced peaks due to Pt⁰ (70.9 eV) and partially oxidized Pt species (72.6 eV). The chemical states of the Pt species were therefore similar for both samples.

However, compared with the Na-free material, the Na-containing Pt/BaTaO₂N sample contained a smaller proportion of metallic Pt and a larger amount of oxidized Pt (Table S2). Interactions between the Na and Pt species can also be inferred from the Na 1s XPS data (Fig. S5). Specifically, the binding energy for the Na 1s peak became larger in the presence of Pt, although it is difficult to determine the exact structure of the Na species because of the small chemical shift and the instability of such species in ambient air.

The present data indicate that the addition of Na ions produced well-dispersed Pt species that were anchored on the BaTaO₂N surface. These Pt species have been reported to function as key active sites that are primarily responsible for hydrogen evolution over Pt/TiO₂ photocatalysts.²⁰⁻²¹ In addition, adsorbed water was present on the Na-containing Pt/BaTaO₂N based on the presence of a peak at 532.2 eV in the O 1s XPS spectrum of this material.²² This peak was not generated by the Na-free Pt/BaTaO₂N sample (Fig. S6). This result suggests that the added Na also stabilized water molecules on the photocatalyst surface. We further analyzed the effect of the Na-containing Pt cocatalyst from the view point of carrier dynamics. Similar to our previous works, the BaTaO₂N samples showed discernable absorption at 15400 cm⁻¹ (649 nm, ~1.9 eV) attributed to photoinduced trapped holes in BaTaO₂N upon photoexcitation as depicted in Fig. S7.^{19,23} The absorbance increased after loading Pt on BaTaO₂N surface, because the number of survived photogenerated holes remaining in BaTaO₂N increased as a result of electron transfer to Pt. Notably, the photoinduced hole lifetime was extended more effectively when the Na-containing Pt cocatalyst was employed, indicating enhanced charge separation or suppressed electron-hole recombination. This is likely because the probability that electrons in BaTaO₂N could reach Pt cocatalyst nanoparticles was greater owing to the high dispersivity of the Pt cocatalyst.

The Na-containing Pt/BaTaO₂N maintained higher H₂ evolution activity than the Na-free Pt/BaTaO₂N through the duration of the reaction (Fig. 1(a)). As shown in Fig. S8, after the reaction, the Pt cocatalyst on the Na-containing Pt/BaTaO₂N was maintained in a highly dispersed state, while the particle size for the Pt cocatalyst was slightly increased on the Na-free Pt/BaTaO₂N. This outcome underlines two points. Firstly, the well-dispersed Pt cocatalyst obtained simply by adding Na very likely enhanced the photocatalytic H₂ evolution reaction. Secondly, the addition of Na stabilized the highly dispersed Pt cocatalyst nanoparticles loaded on the BaTaO₂N during this reaction. XPS data also showed that the presence of Na species stabilized adsorbed water after the reaction (Fig. S5 and S6). In contrast, the effect of the chemical state of the Pt cocatalyst remains unclear. The H₂ evolution rate was found to slow down during the initial 5 h of the reaction, and the original catalytic activity was not recovered even when the H₂ generated during this process was removed (Fig. S9). During this deactivation, the Pt species were reduced to the metallic state regardless of whether the Pt cocatalyst contained Na or not (Fig. 3(b) and 3(d)). In addition, the Na-containing sample had lower and higher proportions of metallic Pt before and after the 5 h reaction, respectively, than the Na-free sample, while exhibiting higher H₂ evolution activity.

The Na-containing Pt/BaTaO₂N also exhibited higher activity than the Na-free Pt/BaTaO₂N during Z-scheme overall water splitting (Fig. 4(a) and 4(b)). As shown in Fig. 4(a), a mixture of Na-containing Pt/BaTaO₂N and H⁺-Cs⁺-modified PtO_x/WO₃ evolved stoichiometric

amounts of H₂ and O₂ from an aqueous NaI solution under visible light. Notably, in contrast to the H₂ evolution reaction from aqueous methanol, only a minor decrease in photocatalytic activity was observed after 12 h. This result suggests that the activity and durability of the Na-containing Pt cocatalyst are sensitive to the specific reactants and to the surrounding environment. Additional research to better understand the active species in highly dispersed Pt cocatalyst nanoparticles will be required to obtain more efficient and stable H₂ evolution using the BaTaO₂N photocatalyst.

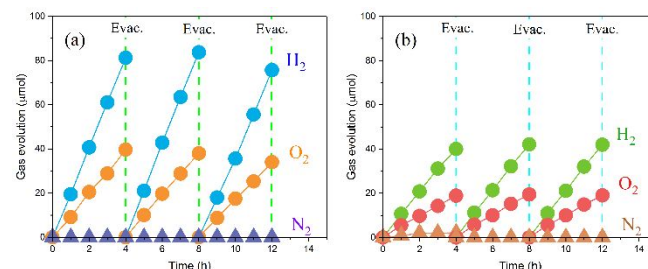


Fig. 4. Time courses of H₂ and O₂ evolution over a mixture of (a) Na-containing and (b) Na-free 0.3 wt% Pt/BaTaO₂N and H⁺-Cs⁺-0.5 wt% PtO_x/WO₃. Reaction conditions: photocatalyst, 100 mg of Na-containing Pt/BaTaO₂N (or Pt/BaTaO₂N) and 200 mg of H⁺-Cs⁺-PtO_x/WO₃; 150 mL of aqueous NaI solution (2 mM); light source, Xe lamp (420 nm < λ < 800 nm). Every four hours, the gas phase of the reaction system was evacuated and Ar gas was introduced to a pressure of 10 kPa.

Conclusions

In summary, this work demonstrated a remarkable improvement in the activity of Pt/BaTaO₂N during the photocatalytic H₂ evolution reaction following the addition of Na as a promoter. The presence of Na improved the dispersion and structural stability of the Pt cocatalyst, leading to more efficient electron extraction from the BaTaO₂N photocatalyst. This technique is expected to provide a new approach to the activation of water splitting photocatalysts responsive to a wide range of visible light, based on refinement of the cocatalyst loading procedure.

Author Contributions

Huihui Li: Conceptualization, Investigation, Data curation, Writing - original draft, Writing - review & editing, Funding acquisition.

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Shanshan Chen: Data analysis.

Takashi Hisatomi: Supervision, Writing - review & editing, Resources, Funding acquisition.

Junie Jhon M. Vequizo: TAS spectra measurement and analysis.

Jiadong Xiao: Data analysis.

Zheng Wang: Data analysis.

Lihua Lin: Data analysis.

Qi Xiao: Data analysis.

Yuliang Sun: Data analysis.

Yugo Miseki: Writing - review

Kazuhiro Sayama: Writing - review
Akira Yamakata: Data analysis, Resources.
Tsuyoshi Takata: Supervision, Resources.
Kazunari Domen: Supervision, Writing - review & editing,
Resources, Funding acquisition.

Conflicts of interest

There are no conflicts to declare.

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