



Photocatalytic reduction of nitrate ions to dinitrogen over layered perovskite $\text{BaLa}_4\text{Ti}_4\text{O}_{15}$ using water as an electron donor



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ABSTRACT

Photocatalytic reduction of NO_3^- to produce NO_2^- , NH_4^+ , and N_2 proceeded on $\text{BaLa}_4\text{Ti}_4\text{O}_{15}$ powder under UV irradiation accompanied with photochemical decomposition of NO_3^- to NO_2^- and O_2 without any sacrificial reagents. Loading of Cu and Ni cocatalysts enhanced the photocatalytic reaction to form N_2 . Ni was the most effective cocatalyst. The $\text{BaLa}_4\text{Ti}_4\text{O}_{15}$ photocatalyst with the Ni cocatalyst loaded by an impregnation method and subsequent H_2 reduction showed high activity for the reduction of NO_3^- to form NO_2^- , NH_4^+ , and N_2 . O_2 also formed as an oxidation product of water. The ratio of the number of reacted electron to that of hole was almost unity, indicating water was consumed as an electron donor for the reduction of NO_3^- . A boric acid of a buffer for pH control was effective to obtain a high yield of N_2 . The N_2 yield reached 85% in the presence of a boric acid after 10 h using a 400 W high-pressure mercury lamp in 10 mmol/L of an aqueous NaNO_3 solution, while it was 50% without the boric acid. The N_2 yield was almost 100% when 3 mmol/L of an aqueous NaNO_3 solution was used with a boric acid.

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1. Introduction

Nitrate ions contained in agricultural and industrial wasted water cause water pollution. Therefore, the development of efficient and clean processes for the elimination of nitrate ions has attracted attention. Electrochemical [1], photocatalytic [2–25], and biological [26] methods have been reported as the candidates for the process as well as a physical separation using a semipermeable membrane [27]. Among them, the photocatalytic process is very simple because just the dispersion of photocatalyst powder can be used: that is the significant advantage for the photocatalytic process. TiO_2 [2–18], ZnO [19], $\text{H}_4\text{Nb}_6\text{O}_{17}$ [6], SrTiO_3 [2,4], $\text{K}_x\text{Ga}_x\text{Sn}_{8-x}\text{O}_{16}$ [20], tantalates [21], CdS [22–24], and Ni-doped ZnS [25] have been reported as photocatalysts for reduction of nitrate ions. ZnO [19] with a wide band gap and CdS [2,22,23] with a visible light response are active photocatalysts for the reduction of nitrate ions to nitrite ions in the presence of reducing reagents

such as methanol without any cocatalysts. TiO_2 , SrTiO_3 , and CdS photocatalysts can produce NH_3 from NO_2^- [2]. Cocatalyst and reaction condition are important for the activity and selectivity of photocatalytic reduction of nitrate ions as for water splitting. For example, when Cu/TiO_2 is used, NH_3 and NO_2^- are obtained in acidic and basic aqueous solutions, respectively [8]. TiO_2 photocatalyst loaded with Cu-Pd alloy cocatalyst gives NH_3 efficiently [13]. Photocatalysts that can reduce NO_3^- to N_2 of a harmless product in the presence of sacrificial reagents are TiO_2 co-loaded with Pd and Cu [8], $\text{TiO}_2\text{:W,N}$ [14], $\text{H}_4\text{Nb}_6\text{O}_{17}$ [6], and $\text{K}_x\text{Ga}_x\text{Sn}_{8-x}\text{O}_{16}$ [20] with UV light responses, and ZnS:Ni [25] with visible light response. However, a clean process should not require any sacrificial reagents. Noble metal cocatalyst-loaded TiO_2 [3–5] and Ni cocatalyst-loaded tantalate [21] photocatalysts reduce NO_3^- in the absence of sacrificial reagents accompanied with O_2 evolution of an oxidation product of water. Among them, Ni-loaded KTaO_3 photocatalyst shows high activity that 44% of NO_3^- can be converted to N_2 after 25 h using a 400 W high pressure mercury lamp [21]. We found that NiO-loaded $\text{BaLa}_4\text{Ti}_4\text{O}_{15}$ photocatalyst with layered perovskite structure shows high activity for water splitting into H_2 and O_2 in a stoichiometric amount [28]. The $\text{BaLa}_4\text{Ti}_4\text{O}_{15}$ photocatalyst powder with a plate-like shape reflecting the layered perovskite structure can be prepared by a polymerizable complex method. When Ag cocatalyst is loaded on the $\text{BaLa}_4\text{Ti}_4\text{O}_{15}$ powder, the photocatalyst is active for CO_2 reduction into CO using water

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Table 1
NO₃⁻ reduction over BaLa₄Ti₄O₁₅ photocatalyst with various cocatalysts.

Cocatalyst (wt%) ^a	Amounts of products after 10 h/μmol				Selectivity ^b %	N ₂ yield ^c %	e ⁻ /h ⁺	
	Reduction product							Oxidation product O ₂
	H ₂	N ₂	NO ₂ ⁻	NH ₄ ⁺				
None	0.3	13	1900	0	1300	99	0.7	0.8
Ni(0.5)	5200	800	210	700	8300	57	45	0.7
Ni(1.0)	3100	790	320	610	7000	68	45	0.7
Ni(2.0)	960	810	960	510	5000	88	46	0.8
Ag(1.0)	1.5	13	2700	0	1300	99	0.7	1.1
Cu(1.0)	78	140	3000	0	2100	97	8	0.9

Catalyst: 0.5 g, solution: 10 mmol L⁻¹ of an aqueous NaNO₃ solution (350–370 mL), a 450 W high pressure mercury lamp, an inner irradiation quartz cell,

^a Loading method of cocatalyst: impregnation and H₂ reduction.

^b (2NO₂⁻ + 8 NH₄⁺ + 10 N₂)/(2H₂ + 2NO₂⁻ + 8 NH₄⁺ + 10 N₂) × 100.

^c (2N₂)/(an initial amount of NO₃⁻) × 100.

as an electron donor [29]. It is interesting to apply this excellent BaLa₄Ti₄O₁₅ photocatalyst to the reduction of NO₃⁻ employing suitable cocatalysts. We preliminary reported the reduction of NO₃⁻ using the BaLa₄Ti₄O₁₅ photocatalyst [30].

In the present study, photocatalytic reduction of NO₃⁻ into N₂ was investigated using the BaLa₄Ti₄O₁₅ photocatalyst loaded with Ni cocatalyst that was effective for tantalate photocatalysts such as KTaO₃. Effects of a H₃BO₃ buffer on the activity and selectivity were examined. The reaction paths were also investigated.

2. Experimental

2.1. Preparation of BaLa₄Ti₄O₁₅ photocatalyst and a loading method of a cocatalyst

BaLa₄Ti₄O₁₅ photocatalyst was prepared by a polymerizable complex method according to the previously reported procedure [28,29]. BaCO₃ (Kanto chemical; 99.0%), Ti(OC₄H₉)₄ (Kanto chemical; 97.0%), La(NO₃)₃·6H₂O (Wako; 99.9%), propylene glycol (Kanto chemical; 99.0%), and citric acid (Sigma Aldrich; 99.0%) were used as starting materials. An aqueous Ni(NO₃)₂ solution containing the photocatalyst was evaporated to dryness and the resulting solid was calcined at 543 K in air. Reduction treatment was performed in the presence of 200 Torr of H₂ gas at 773 K for 2 h to obtain metallic Ni cocatalyst-loaded BaLa₄Ti₄O₁₅ photocatalyst.

2.2. Characterization

The photocatalyst was identified as a single phase by powder X-ray diffraction (Rigaku; Miniflex, Cu Kα). Scanning electron microscopy (SEM) images were taken using a JEOL JSM-6700F.

2.3. Photocatalytic reaction

Photocatalytic NO₃⁻ reduction was carried out in a gas-closed circulation system using an inner irradiation quartz cell containing 350–370 mL of an aqueous NO₃⁻ suspension of the photocatalyst (0.5 g). pH was controlled by an addition of H₃BO₃ into the suspension, if needed. A 400 W high-pressure mercury lamp was used as a light source. Gaseous products of H₂, O₂, and N₂ were determined by a gas chromatograph (Shimadzu, GC-8A) with a thermal conductivity detector (MS-5A, Ar carrier). NO₃⁻ of a reactant, and NO₂⁻ and NH₄⁺ of products were analyzed by an ion chromatograph (TOA-DKK, ICA-2000, DS-plus, columns for cations and anions: PCI-302S and PCI-230, eluents for cations and anions: 4 mmol/L of HNO₃aq. (pH 2.4) and a mixed solution of 0.8 mmol/L of Na₂CO₃aq. and 2.4 mmol/L of NaHCO₃aq. (pH 9.9)).

3. Results and discussion

3.1. Photocatalytic reduction of NO₃⁻ over BaLa₄Ti₄O₁₅ photocatalyst

Table 1 shows NO₃⁻ reduction over BaLa₄Ti₄O₁₅ photocatalyst with various cocatalysts. Naked BaLa₄Ti₄O₁₅ photocatalyst gave NO₂⁻ and O₂. This is mainly due to not photocatalytic but photochemical reaction under UV irradiation (λ < 300 nm) [21]. A significant decrease in NO₂⁻ and increases in N₂, NH₄⁺, and H₂ were observed when Ni cocatalyst was loaded by an impregnation method and subsequent H₂ reduction. The activity depended on the loading amount of the Ni cocatalyst. The maximum N₂ yield and maximum total amounts of reacted electrons and holes were obtained at 0.5 wt% of the Ni cocatalyst. N₂, NH₄⁺, and H₂ were formed by photocatalytic reactions, whereas NO₂⁻ formed by not only photocatalytic but also photochemical reactions.

Ag cocatalyst did not give any significant effect on the photocatalytic NO₃⁻ reduction, although NO₂⁻ formation was enhanced. N₂ formation was enhanced on Cu cocatalyst-loaded BaLa₄Ti₄O₁₅ photocatalyst compared with naked BaLa₄Ti₄O₁₅. Although Cu cocatalyst gave a large amount of NO₂⁻ than Ni cocatalyst, formations of N₂ and NH₄⁺ were suppressed as well as H₂ formation. The behaviors for NO₂⁻ and NH₄⁺ formations on the Cu cocatalyst-loaded BaLa₄Ti₄O₁₅ photocatalyst were similar to those on Cu/TiO₂ in a basic aqueous solution [8]. These results were due to a large overpotential of Cu toward H₂ formation.

Ni cocatalyst that was loaded by an impregnation method and subsequent H₂ reduction showed high performance for the BaLa₄Ti₄O₁₅ photocatalyst. The high performance of the BaLa₄Ti₄O₁₅ photocatalyst is due to its high conduction band level, anisotropic crystal structure that enhances charge separation as observed for water splitting, and the suitable combination with a Ni cocatalyst. Kominami and co-workers have reported a high performance for N₂ formation on metal-loaded TiO₂ by NO₃⁻ and NO₂⁻ reduction in the presence and absence of a hole scavenger [16–18]. These reactions are not accompanied with O₂ evolution, because the hole scavenger and NO₂⁻ are oxidized instead of H₂O molecules. This is the significant difference between the TiO₂ and BaLa₄Ti₄O₁₅ systems. Although O₂ evolution is observed for NO₃⁻ reduction using Pt/TiO₂ photocatalyst, the main reduction product is NH₃ [3]. So, BaLa₄Ti₄O₁₅ is a unique photocatalyst for NO₃⁻ reduction as well as some tantalates [21].

3.2. Effect of pH on photocatalytic NO₃⁻ reduction over BaLa₄Ti₄O₁₅

pH of a reactant solution changed from 7 to 12 after 10 h of a photocatalytic reaction time. The change in pH was mainly

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