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Introduction

Methane (CH₄) is a ubiquitous substance obtained from underground and biomass. Considering it as a carbon resource and not as a fuel, the conversion of methane to other industrially valuable chemical compounds such as carbon monoxide (CO) and hydrogen (H₂) is very attractive to researchers.^{1–7} The mixture of CO and H₂ known as syngas could be catalytically obtained in steam reforming of methane (SRM, eqn (1)). For the industrial production of hydrogen, successive water gas shift reaction of CO gives additional H₂ and CO₂ (WGS, eqn (2)) and the overall reaction gives hydrogen and CO₂ without CO production (eqn (3)).

$$CH_4 + H_2O \rightarrow CO + 3H_2$$
 $\Delta G_{298K}^{\circ} = 142.1 \text{ kJ mol}^{-1}$ (1)

$$CO + H_2O \rightarrow CO_2 + H_2$$
 $\Delta G_{298K}^{\circ} = -28.6 \text{ kJ mol}^{-1}$ (2)

Carbon monoxide as an intermediate product in the photocatalytic steam reforming of methane with lanthanum-doped sodium tantalate[†]

Wirya Sarwana,^{ab} Akihiko Anzai,^a Daichi Takami,^a Akira Yamamoto ^{(D)ac} and Hisao Yoshida ^{(D)*ac}

Photocatalytic steam reforming of methane (PSRM) has been studied as an attractive method to produce hydrogen by utilizing photoenergy like solar energy at around room temperature with metal-loaded photocatalysts, where methane and water are selectively converted to carbon dioxide and hydrogen. In the present study, we used a PSRM system using a flow reactor at around room temperature to yield the partially oxidized product, carbon monoxide (CO). It was found that some La-doped NaTaO₃ samples can produce carbon monoxide constantly in addition to hydrogen and carbon dioxide. Among the prepared samples, a La(2 mol%)-doped NaTaO₃ photocatalyst without any cocatalyst exhibited the highest photocatalytic activity and the highest CO selectivity of 24%. The CO yield depended on the photocatalysts and the reaction conditions. Suitable reaction conditions for CO yield were high light intensity, a higher flow rate, and a moderately high methane/water ratio. Some additional reaction tests revealed that water gas shift (WGS) can take place as an undesirable successive reaction, *i.e.*, the produced carbon monoxide can successively react with water to form carbon dioxide, which would restrict the CO yield significantly.

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 \quad \Delta G^{\circ}_{298K} = 113.5 \text{ kJ mol}^{-1}$$
 (3)

These reactions are highly endergonic except for WGS and need a huge amount of energy. Conventionally, methane combustion supplies heat for the required energy and thus the reaction temperature increases, which necessitates several requirements such as inhibition of carbon deposition and an expensive heat-resistant reactor. Therefore, a new reaction system that can work at low temperature is highly desirable for these endergonic reactions.

Photocatalytic reactions have been shown as a promising way to promote thermodynamically difficult reactions by utilizing solar light as photoenergy and thus the reaction can occur even at room temperature. Photocatalytic steam reforming of methane (PSRM) can convert CH₄ and H₂O directly to H₂ and CO₂ (eqn (3)) even under mild conditions although it is endergonic.^{8,9} This reaction was originally developed by our group using a Pt-loaded TiO₂ (Pt/TiO₂) photocatalyst^{10,11} and a Pt-loaded La-doped NaTaO₃ photocatalyst (Pt/NaTaO₃:La).^{10,12,13} After that, various photocatalysts have also been reported for the PSRM such as Pt/CaTiO₃,^{14,15} Pt/CaTaO₃:La,¹⁶ Rh/K₂Ti₆O₁₃,^{17,18} and Pt/β-Ga₂O₃.¹⁹⁻²¹ These studies have focused only on hydrogen production, where the observed molar ratio has been always H₂/CO₂ = 4 (eqn (3)).

So far, photocatalytic conversion of methane and water has been reported also for the production of valuable



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^a Graduate School of Human and Environmental Studies, Kyoto University, Kyoto 606-8501, Japan. E-mail: yoshida.hisao.2a@kyoto-u.ac.jp

^b Department of Mechanical Engineering, Sumbawa University of Technology, Olat Maras, Sumbawa, West Nusa Tenggara, 84371, Indonesia

 $[^]c$ Elements Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto University, Kyoto 615-8520, Japan

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chemicals such as methanol,^{22–27} ethanol,²⁸ and aldehydes.²⁹ In the present study, we attempted to change the selectivity of the PSRM to produce CO that is one of the partially oxidized products from methane and very valuable as a chemical intermediate. In the previous study, we found that a metal cocatalyst could change the product selectivity in PSRM. The Rh cocatalyst loaded either on the $K_2Ti_6O_{13}$ surface or the NaTi₆O₁₃ surface always gave H₂ and CO₂ selectively without any formation of CO.^{18,30} In contrast, a Pt loaded photocatalyst gave CO as a minor by-product with a low selectivity of 9–10% over Pt/K₂Ti₆O₁₃ (ref. 18) and Pt/Ga₂O₃ (ref. 31) photocatalysts. There has been, however, no report focusing on CO production in the PSRM.

Here, we report the PSRM to produce CO by using a Ladoped NaTaO₃ (NaTaO₃:La) photocatalyst without loading any cocatalysts, where the CO selectivity among the oxidative products reached 24% for the first time. It is also revealed that the low CO selectivity is due to the successive oxidation to CO_2 ; in other words, CO is an intermediate product in the PSRM.

Experimental

Catalyst preparation

Sodium tantalate (NaTaO3, referred to as NTO) and lanthanum-doped sodium tantalate samples (NaTaO3:La, referred to as NTO:La) were mainly prepared by a flux method. The starting materials, Na₂CO₃, Ta₂O₅ (Rare Metallic, 99.99%), and La₂O₃ (Kishida, 99.99%), were mixed together with a flux, NaCl (Kishida, 99.5%), in an alumina mortar for 15 min. The molar ratio for NaTaO3:La was Na: Ta:La = 100:100:x, where x is from 0 to 5, and the solute concentration in the molten mixture was 70%, i.e., the ratio was $NaTaO_3$: NaCl = 70: 30. The mixture was placed in a platinum crucible and heated by using an electric muffle furnace, where the temperature was increased at 200 K h⁻¹ from room temperature to 1273 K and kept for 5 h. It was cooled down at 100 K h⁻¹ to 773 K, and naturally to ambient temperature in the furnace. The product obtained was washed with hot distilled water (353 K, 500 ml) 3 times to remove the flux and then dried at 353 K overnight. These samples were labelled NTO:La(x), where x is the amount of La (mol%) used as a dopant.

Another sample was prepared by a solid-state method with the same procedure as mentioned above only without using the NaCl flux. The La doping was 2 mol%. The starting materials were mixed, heated, and cooled, followed by washing under the same conditions as mentioned above. This sample was referred to as NTO:La(2)SS.

Some precious metals such as Au, Ag, Pd, and Pt and transition metals such as Ni, Cu, and Zn were loaded as cocatalysts on the NTO:La surface by an impregnation method. The precursors used for the loading process were HAuCl₄·6H₂O, AgNO₃ (Kishida, 99.8%), PdCl₂ (Kishida, 99%), H₂PtCl₆ (Wako, 99.9%), Ni(NO₃)·6H₂O (Wako, 99%), Cu(NO₃)₂·3H₂O, and Zn(NO₃)₂·6H₂O (Nacalai Tesque, 99%).

The NTO:La samples (2 g) were soaked and stirred in an aqueous solution of the precursor (100 ml; 0.05, 0.1 or 1 mM at 353 K) until the water completely evaporated, and dried overnight in an oven at 353 K. Before use, metal loaded NTO: La was calcined at 673 K for 2 h. This was denoted M(y)/NTO: La where y is the wt% of the metal cocatalyst. To investigate the role of La doping, two additional La loaded samples were also prepared. The precursor used for the loading process was La(NO₃)₃·6H₂O (Nakalai Tesque, 99.9%). The 0.3 wt% La species was loaded on the surface of the NTO and NTO:La(1) samples by the impregnation method, and these samples were labelled La(0.3)/NTO and La(0.3)/NTO:La(1).

Some photocatalysts such as Ga_2O_3 (Kojundo, 99.99%), ZnO (Kojundo, 99.99%), and TiO₂ (Ishihara Sangyo Kaisha, ST-01, 300 m² g⁻¹) were also employed for comparison. All of these photocatalysts were used as received without any pretreatment.

Characterization

The content of La in the samples was determined by X-ray fluorescence (XRF) analysis on an EDX-8000 (Shimadzu) with a calibration curve obtained using the samples prepared by a conventional impregnation method.

The scanning electron microscopy (SEM) images were captured using a JEOL JSM-890. The average particle size was evaluated from the SEM images.

X-ray diffraction (XRD) patterns of the samples were recorded at room temperature using a Shimadzu Lab X XRD-6000. The radiation used was Cu K α (40 kV, 30 mA). The crystallite size was determined by the Scherrer equation using the full width at half maximum (FWHM) of the diffraction line at $2\theta = 22.8^{\circ}$ in the XRD patterns.

The BET specific surface area was measured by using the adsorbed amount of N_2 on the sample surface at 77 K using a Quantachrome Monosorb MS-21.

The diffuse reflectance (DR) UV-visible spectra were recorded using a JASCO V-670 equipped with an integrating sphere, where $BaSO_4$ was used as a reference. The bandgap was estimated by using a Tauc plot.³²

Photocatalytic activity test

Photocatalytic reaction tests for the PSRM were carried out using a fixed bed flow reactor as shown in Fig. S1.⁺¹³ The photocatalyst powder was pressed under 40 MPa for 1 min, which gave a pellet. The pellet obtained was crushed and sifted using 25 mesh and 50 mesh sieves. The remaining granules on the 50 mesh sieve were used for the reaction tests. The catalyst granules (1.2 g) were introduced inside a quartz reactor ($60 \times 20 \times 1 \text{ mm}^3$), where the irradiated area of the photocatalyst was 6.0 cm². The feed gas mixture used for this reaction test typically consisted of CH₄ (25%) and H₂O (2.4%) with argon as a carrier gas. The flow rate of the feed gas was 15 ml min⁻¹. A 300 W xenon lamp (PE300BUV) was used as a light source for photoirradiation without any optical filter. The light intensity was 165 mW cm⁻² that was

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Results and discussion

Characterization of the photocatalysts

Fig. 1 shows the SEM images of the non-doped NTO and various NTO:La samples prepared by the flux method and the solid-state reaction method. The average particle sizes of these samples estimated from these images are listed in Table 1. The non-doped NTO sample prepared by the flux method consisted of roundish cubic particles sized in the range of 0.2-2.5 µm (Fig. 1a), where the average particle size was 0.8 µm (Table 1). The La-doped samples prepared by the flux method showed cubic crystals sized in the range of 0.04-1.0 µm (Fig. 1b-e), and the average particle sizes were 0.21-0.55 µm, which were much smaller than those of the nondoped NTO sample. This result confirmed that La doping can inhibit the crystal growth of NaTaO₃.³³⁻³⁵ The NTO:La(1) sample showed the smallest average particle size of 0.21 µm. However, the NTO:La(5) sample with the higher La doping showed a slightly different morphology with a larger size of



Fig. 1 SEM images of the prepared samples: (a) non-doped NTO, (b) NTO:La(0.5), (c) NTO:La(1), (d) NTO:La(2), (e) NTO:La(5), and (f) NTO: La(2)SS.

0.55 μ m (Fig. 1e). As for the NTO:La(2)SS sample, the morphology of the crystal was more roundish with somewhat irregular shapes (Fig. 1f). These results are also quite similar to the previous report.¹³

Fig. S2[†] shows the XRD patterns of the non-doped NTO and various NTO:La samples. The diffraction lines of all the samples indicate the presence of the NaTaO₃ perovskite phase. No impurity phases related to La2O3 or La were detected, although this might be due to the low concentration of the La dopant. The average crystallite sizes of each sample were estimated and are listed in Table 1. As shown, the more La dopant introduced into NaTaO₃, the smaller the crystallite size obtained. The NTO:La(2)SS sample had a similar crystallite size to the other NTO:La samples with low La doping such as the NTO:La(0.5) and NTO:La(1) samples. Note that the crystallite sizes determined by XRD were much smaller than the particle size observed in the SEM images (Table 1). This means that the crystals observed in the SEM images were not single crystals but polycrystals.^{13,16} In the NTO:La(2) and NTO:La(5) samples, the crystallite size decreased with increasing La doping while the particle size increased. It is suggested that the larger amount of La ions enhanced the aggregation of the particles of the smaller crystallites.

The BET specific surface areas of the various samples are also listed in Table 1. As shown, the NTO:La(1) sample has the highest specific surface area compared to the other samples, supporting that doped lanthanum cations inhibit the crystal growth thus increasing the specific surface area. The increase of the specific surface area was consistent with the increasing La-doping amount in the range of 0–1 mol%. However, in the case of the NTO:La(2) and NTO:La(5) samples, the specific surface areas decreased with increasing La doping, suggesting that the aggregation of the particles decreased the specific surface area. Sun *et al.* reported that a higher Sr doping amount in NaTaO₃ samples could decrease the surface area.³⁶

Simply stated, the surface area should be inversely proportional to the particle size. Thus, we examined the relationship between the specific surface area and the average particle size based on the values of the samples with 0–1% La (Table 1) and we confirmed an inversely proportional correlation (Fig. S3†). Such correlation was not obtained between the specific surface area and the crystallite size. This means that the BET specific surface area reflects the surface area of the polycrystal particles observed in the SEM images, not the crystallite size. It was found that the specific surface areas for the NTO:La(2) and NTO:La(5) samples were higher than expected based on the correlation, suggesting that the aggregation provides interspaces between the particles as a certain pore structure in the NTO:La(5) sample.

These powder samples were pelletized to form granules for the photocatalytic reaction tests. In some cases, the specific surface areas of the granule samples were lower than those of the powder samples but not significantly decreased (Table 1).

Table 1 Structural and optical properties of the prepared samples

Entry	Sample	La content ^{<i>a</i>} (mol%)	Average particle size ^b (µm)	Crystallite size ^c (nm)	$S_{\text{BET powder}} d (\text{m}^2 \text{g}^{-1})$	$S_{\text{BET granule}}^{s} \left(m^2 g^{-1} \right)^e$	Bandgap ^f (eV)
1	NTO	0.0	0.79	68	2.4	1.9	4.0
2	NTO:La(0.5)	0.3	0.29	50	5.3	5.4	4.1
3	NTO:La(1)	0.7	0.21	42	8.3	7.7	4.1
4	NTO:La(2)	1.7	0.25	35	7.5	7.4	4.1
5	NTO:La(5)	4.8	0.55	27	5.6	5.5	4.1
6	NTO:La(2)SS	1.5	0.41	43	4.1	3.9	4.1

^{*a*} The actual La dopant content measured by XRF. ^{*b*} The average particle size estimated from the SEM images. ^{*c*} The average crystallite size calculated from a line width in the XRD patterns. ^{*d*} The specific surface area of the powder sample measured by the BET method. ^{*e*} The specific surface area of the granule samples measured by the BET method. ^{*f*} The bandgap estimated by a Tauc plot from the DR UV-vis spectra.

The DR UV-visible spectra of the samples are shown in Fig. S4.[†] The bandgaps of each sample were calculated by using a Tauc plot and are listed in Table 1. These results suggest that La doping can enlarge the bandgap of NaTaO₃, which is consistent with the previous report.¹³

Photocatalytic activity test

Fig. 2 shows the time course of the product formation rates in the photocatalytic reaction test for the PSRM with the NTO:La(2) sample in the flow of feed gas (25% CH₄, 2.4% H₂O and 72.6% Ar) at atmospheric pressure and room temperature. Although the production rates of H₂ and CO₂ decreased slightly for the initial 4 hours, the production rates of H₂ and CO₂ became constant at 21 and 4 µmol h⁻¹, respectively. It was found that CO was also produced in the addition of H₂ and CO₂. The CO production rate was constant from the start at 1 µmol h⁻¹. Other gaseous oxidation products such as ethane were not detected with the



Fig. 2 Time course of the production rate of H₂ (diamonds), CO₂ (squares), and CO (black circles) and $R(e^{-}/h^{+})$ (white circles) that is the consumed electron/hole ratio calculated from the production rates. The NTO:La(2) photocatalyst (1.2 g) was used in a flow of the gas mixture (25% CH₄, 72.6% Ar, and 2.4% steam) at the flow rate of 15 ml min⁻¹ under photoirradiation. The light intensity used was 165 mW cm⁻² when measured at 254 ± 10 nm.

online GC-TCD. The product formation rates and the product selectivity were constant and the reaction continuously proceeded for a long time, for at least 20 hours. The ratio of photoexcited electrons and holes that were consumed for the product formation, $R(e^{-}/h^{+})$, was estimated from the formation rates of H₂, CO, and CO₂, which are R_{H_2} , R_{CO} , and R_{CO_2} , respectively, according to eqn (4). As shown in Fig. 2, this ratio was almost unity, $R(e^{-}/h^{+})$ = 1, meaning that the products should be almost limited to H₂, CO, and CO₂. Based on these results, the CO selectivity among the oxidative products, $S_{CO}(\%)$, can be calculated according to eqn (5) and the CO selectivity was as high as 24% with the NTO:La(2) photocatalyst. The apparent quantum efficiency, AQE (%), defined as the ratio of the number of photons used for H₂ formation to the number of incident photons that can be absorbed by the photocatalyst, was estimated to be 0.12%. No products were obtained under dark conditions or without employing а photocatalyst. These facts obviously indicate that the reaction takes place photocatalytically.

$$R(e^{-}/h^{+}) = R_{H_2}/(3 \times R_{CO} + 4 \times R_{CO_2})$$

$$\tag{4}$$

$$S_{\rm CO}(\%) = 100 \times R_{\rm CO} / (R_{\rm CO} + R_{\rm CO_2})$$
 (5)

Fig. 3 shows the photocatalytic activity of the various samples. All the prepared La-doped NaTaO₃ samples without any cocatalysts showed photocatalytic activity to produce CO in the PSRM. As shown in Fig. 3A, the NTO:La(x) samples exhibited higher photocatalytic activities to produce H₂, CO, and CO₂ than the non-doped NTO sample (Fig. 3Aa-e). It is confirmed that La doping could increase the photocatalytic activity of NaTaO₃.^{12,33} Among them, the NTO:La(0.5), NTO: La(1), and NTO:La(2) samples exhibited the highest photocatalytic activity, e.g., NTO:La(2) exhibited production rates of 23 $\mu mol~h^{-1}$ for $H_2,~1~\mu mol~h^{-1}$ for CO, and 4 μmol h^{-1} for CO₂ (Fig. 3Ad). The NTO:La(2)SS sample also showed high production rates (Fig. 3Af) but they were lower compared to the NTO:La(2) sample (Fig. 3Ad). This result reveals that the sample prepared by the flux method has better photocatalytic activity in the PSRM, which is quite similar to the previous report.¹³ The ratios of the electrons



Fig. 3 (A) Production rates of H₂ (gray bar), CO (black bar), and CO₂ (white bar) and the ratio of the consumed electrons and holes (white circle) in the various samples: (a) NTO, (b) NTO:La(0.5), (c) NTO:La(1), (d) NTO:La(2), (e) NTO:La(5), and (f) NTO:La(2) SS. (B) Enlarged graph showing the CO and CO₂ production rates and the CO selectivity, S_{CO} (white triangle). (C) Photocatalytic production rates and CO selectivity with another series of samples on which a La oxide species was loaded by the impregnation method: (a) NTO, (b) La(0.3)/NTO, (c) NTO:La(1), (d) La(0.3)/NTO:La(1), and (e) Pt(0.1)/NTO:La(1). Photocatalyst: 1.2 g. Photoirradiation area: 6 cm². The feed gas consists of 25% CH₄, 72.6% Ar, and 2.4% steam (total flow rate: 15 ml min⁻¹). Light intensity: 165 mW cm⁻² for (A) and (B) and 27 mW cm⁻² for (C). Sampling was carried out after 4 hours irradiation.

and holes consumed for all the samples were almost unity except for the NTO:La(5) sample (Fig. 3Ae). The unbalance of

electron and hole consumption in the NTO:La(5) sample might be caused by the production of some undetected oxidative products, such as coke.

To compare the CO production rate and selectivity, the enlarged graph is shown in Fig. 3B. The NTO:La(x) and NTO: La(2)SS samples produce CO as a minor product. The Ladoped samples showed a higher CO production rate than the non-doped NTO sample although the NTO:La(5) sample exhibited a low CO production rate among them. However, the CO selectivity with each photocatalyst was in the range of 15% to 24%, meaning that the CO selectivity did not vary so much with the amount of La dopant. Meanwhile, the non-doped NTO sample could not produce CO.

In order to investigate the role of La doping in crystals, another series of samples were prepared, i.e., a La oxide species was loaded on the surface of the non-doped NTO and NTO: La(1) samples, and they were used for the photocatalytic reaction test (Fig. 3C). Although the photocatalytic H₂ production rate over the NTO sample was 1.26 μ mol h⁻¹ (Fig. 3Ca), that over the La(0.3)/NTO sample was 0.53 μ mol h⁻¹ (Fig. 3Cb), meaning that the La oxide species on the NTO surface decreased the photocatalytic activity to less than half its original value. This negative effect was also observed over the NTO:La(1) sample (Fig. 3C, c and d). These results suggested that the surface La oxide species would change the properties of the photocatalytic active sites, decreasing the photocatalytic activity. Thus, the La doping effect on the photocatalytic activity of the NTO:La photocatalysts should be generated by the La³⁺ cations incorporated in the crystal structure and not by the La oxide species located on the surface. Onishi et al. reported that the electron-hole recombination process was suppressed by La doping in the NaTaO₃ host.^{38,39} The gradient of electrostatic potential due to La doping promotes more efficient charge separation.³⁸ However, the photocatalytic activity of the NTO: La(5) sample was almost the same as that of the bare NTO sample (Fig. 3A, a and e), which is also consistent with the literature.³⁸ The excess La dopant in NaTaO₃ might produce the La oxide species on the surface, decreasing the photocatalytic activity.

To know the effect of metal cocatalysts, various metal loaded NTO:La(1) samples were examined as listed in Table S1.† These metal loaded samples exhibited lower photocatalytic activity for CO production than the bare NTO: La(1) sample. The addition of a Pt cocatalyst on the NTO: La(1) sample increased the hydrogen production rate but suppressed CO formation, which is consistent with the previous study. Loading a Pd cocatalyst also could change the photocatalyst selectivity. Since the NTO:La(1) sample without any loaded cocatalysts could produce H₂, CO, and CO₂, it is demonstrated that the surface sites of the bare NTO:La photocatalyst could originally produce H₂, CO, and CO₂ and Pt and Pd cocatalysts only promote the formation of H₂ and CO₂.^{10-14,16,37} It is usually considered that Pt can function as a good cocatalyst to enhance the electron and hole separation and thus enhance the photocatalytic activity.13-16,40,41 Thus, even if the photocatalyst produces CO, the Pt metal cocatalyst

might promote successive conversion of CO with H_2O to form CO_2 . On the other hand, the other metal species such as Ag, Ni, Cu, and Zn show negative effects on both the photocatalytic activity and CO selectivity (Table S1†). These cocatalysts would interact with the surface active sites of the bare photocatalyst and make them less reactive.

As a comparison, we also checked the photocatalytic activity and CO selectivity of some other photocatalyst samples such as Ga_2O_3 , TiO_2 , and ZnO as listed in Table S1[†] entries 10–12. These samples were used directly without any additional pretreatment. As a result, NTO:La(1) exhibited the highest photocatalytic activity and CO selectivity among them. The Ga_2O_3 sample also showed photocatalytic activity to produce H_2 , CO, and CO₂ with a high CO selectivity, 19%. In contrast, non-doped NTO, ZnO and TiO₂ showed low photocatalytic activities for H_2 and no CO or CO₂ formation.

Reaction scheme for CO production

To elucidate the possibilities of the successive reactions of produced CO_2 to give CO, such as photocatalytic dry reforming of methane (PDRM, eqn (6)) and photocatalytic reverse water gas shift (PRWGS, eqn (7)), we performed photocatalytic reaction tests with the NTO:La(1) photocatalyst.

$$CO_2 + CH_4 \rightarrow 2CO + 2H_2 \quad \Delta G_{298K}^{\circ} = 170.7 \text{ kJ mol}^{-1}$$
 (6)

$$CO_2 + H_2 \rightarrow CO + H_2O$$
 $\Delta G_{298K}^{\circ} = 28.6 \text{ kJ mol}^{-1}$ (7)

In the PDRM experiment, the concentration of CO_2 in the feed gas mixture was 20%, that of CH_4 was 20% and the rest was Ar gas, while in the PRWGS experiment the composition of the feed gas was 20% CO_2 , 20% H_2 , and 60% Ar gas. Although this CO_2 concentration was much higher than that achieved in the PSRM reaction experiments in this study, there were no gaseous products in both reactions, meaning that these reactions did not take place successively. Although CO_2 reduction using water as an electron source is another probable reaction, Nakanishi *et al.* already reported that La doped NaTaO₃ without a cocatalyst was not active for producing CO through CO_2 reduction with water.⁴²

On the other hand, to elucidate the successive reaction of produced CO with water, the tests for photocatalytic watergas shift (PWGS, eqn (2)) were carried out with various NTO and NTO:La photocatalysts (Fig. 4), where the feed gas mixture consisted of 15% CO, 2.7% H₂O, and 82.3% Ar. Under dark conditions, there were no H₂ and CO₂ observed (not shown). However, upon light irradiation, the gaseous products were clearly detected. It was found that the WGS can occur photocatalytically under these conditions with these photocatalysts. The ratio of the products, $R_{\text{WGS}}(e^-/h^+)$, was estimated by using eqn (8) where R_{H_2} and R_{CO_2} are the production rates for H₂ and CO₂, respectively.

$$R_{\rm WGS}(e^{-}/h^{+}) = R_{\rm H_2}/R_{\rm CO_2}$$
 (8)



Fig. 4 Production rate of H₂ (gray bar) and CO₂ (white) and $R_{WGS}(e^{-1}/h^+)$ (open circle) in the photocatalytic water gas shift (PWGS) reaction test over the samples: (a) bare NTO, (b) NTO:La(1), (c) NTO:La(2), and (d) NTO:La(5). Photocatalyst: 1.2 g, photoirradiation area: 6 cm², reactant: 15% CO, 2.7% H₂O and Ar as the balance, flow rate: 15 ml min⁻¹. Sampling was carried out after 2 hours irradiation.

In the PWGS experiment, the ratio of the consumed electrons and holes was unity with these samples, which is consistent with eqn (2). These photocatalysts, especially the NTO:La photocatalysts, were highly active for the photocatalytic WGS (PWGS). These high production rates would be related to the lower reaction Gibbs energy for the WGS. It is known that the steam reforming of methane (SRM) is a highly endergonic reaction while the water gas shift (WGS) is an exergonic reaction as mentioned above (eqn (2) and (3)). This result revealed that the photocatalytic water gas shift can occur in the photocatalytic steam reforming of methane (PSRM) with the NTO and NTO:La photocatalysts and the latter is more active. This is the first report that a bare semiconductor photocatalyst without a cocatalyst promotes water gas shift (WGS) with high selectivity.

These results suggest that CO was produced in the photocatalytic steam reforming (PSRM, eqn (1)) and converted to CO_2 in the photocatalytic water gas shift reaction (PWGS, eqn (2)). This provides a steady state for the CO production, which is the reason why the CO selectivity was low being 15–24% in the present system. Further, the successive reaction of CO_2 with CH_4 (PDRM, eqn (6)) and H_2 (PRWGS, eqn (7)) to produce CO could scarcely take place under the present conditions as mentioned. Thus, the proposed scheme for CO production is summarized in Scheme 1. If the successive PWGS can be controlled by the development of photocatalysts or reaction conditions, higher CO selectivity will be obtained.

Reaction conditions

The influence of the reaction conditions, such as the light intensity, the flow rate of reactants, and the CH_4 concentration, on the photocatalytic activity and the CO

$$CH_4 \xrightarrow{H_2O} CO + 3H_2 \xrightarrow{H_2O} CO_2 + 4H_2$$
$$2CO + 2H_2 \xrightarrow{\leftarrow} CO_2 + CH_4$$
$$CO + H_2O \xrightarrow{\leftarrow} CO_2 + H_2$$

Scheme 1 Proposed reaction scheme for CO production in the photocatalytic steam reforming of methane over a $NaTaO_3$:La photocatalyst based on the experimental results.

selectivity was also investigated. Fig. 5A shows the effect of the irradiation light intensity on the photocatalytic performance of the NTO:La(2) photocatalyst, where the light intensities utilized were 27, 35, and 165 mW cm⁻² without using an optical filter, which represent incident photon numbers of 1.1 \times $10^{18},$ 1.4 \times $10^{18},$ and 6.6 \times 10^{18} $s^{-1},$ respectively. As mentioned, no reaction occurred in the dark. Higher light intensity provides higher production rates, which is quite reasonable for photocatalysis. Interestingly, it was found that the CO selectivity also slightly increased with increasing light intensity from 18% to 24%. It is suggested that the CO selectivity should be related to the difference of the reaction rates of the first PSRM (eqn (1)) and the successive PWGS (eqn (2)). As shown in eqn (1), it required 6 pairs of electrons and holes to promote CO generation in the PSRM, while the PWGS only needs 2 pairs of charge carriers. By increasing the light intensity, more electrons and holes will be available for these photocatalytic reactions, which might be more critically beneficial to the first PSRM reaction rather than the successive PWGS reaction, resulting in the higher CO formation rate. Higher temperature originating from the high light intensity might also be another possibility for increasing CO selectivity since the PSRM is an endothermic reaction while PWGS is exothermic.

Fig. 5B shows the effect of the increasing total flow rate of the reaction mixture (15, 30, and 50 ml min⁻¹), which decreases the contact time (2.4, 1.2, and 0.7 s, respectively), on the methane conversion and the CO selectivity over the NTO:La(2) photocatalyst. As expected, the methane conversion decreased with the increasing flow rate because of less contact time. The CO₂ production rate decreased with the increasing flow rate (Fig. S5A[†]), while the CO production rate was observed to be almost the same for various flow rates, resulting in a slightly higher CO selectivity at the highest flow rate. In principle, a high flow rate with a short contact time should lower both the reaction rates, the CH₄ conversion to CO (eqn (1)) and the successive reaction of CO to CO_2 (eqn (2)). In the present case, it was revealed that a short contact time can further limit the successive reaction of CO to CO_2 because practically there is less contact time for the successive reaction. It is concluded here that contact time limitation can slightly increase the CO selectivity.

Fig. 5C and S5B[†] show the effect of the composition of the feed gas mixture on the photocatalysis with the NTO: La(1) photocatalyst, where the CH₄ concentration was varied with a constant H₂O concentration to provide various ratios of CH₄ to H₂O. The ratios of CH₄/H₂O examined were from



Fig. 5 Formation rate of CO (circle), CO₂ (square), and H₂ (diamond) together with CO selectivity (triangle) and CH₄ conversion (asterisk) under different reaction conditions: (A) various incident photon numbers; flow rate, 30 ml min⁻¹; feed gas composition: CH₄ (35%), steam (2%), and Ar (balance); photocatalyst, the NTO:La(2) sample, (B) various flow rates of the feed gas mixture: 15, 30, and 50 ml min⁻¹; light intensity, 35 mW cm⁻²; feed gas composition: CH₄ (35%), steam (2%), and Ar (balance); photocatalyst, the NTO:La(2) sample, and (C) various CH₄/H₂O ratios in the feed gas: CH₄ (10–40%), steam (1.9–2.8%), and Ar (balance); light intensity, 165 mW cm⁻²; flow rate, 15 ml min⁻¹; photocatalyst, the NTO:La(1) sample. The mass of photocatalyst used was 1.2 g and the irradiation area was 6 cm² for each experiment. See also Fig. S5 in the ESI;†

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3.5 to 21, much higher than the CH_4/H_2O stoichiometric ratio, 0.5. The graph shows that by increasing the CH_4/H_2O ratio, the CH₄ conversion decreased gradually and became stable. The CO selectivity increased in the lower range of the CH₄/H₂O ratio from 3.5 to 11, and became constant at the higher ratio range. Water would be strongly adsorbed on the photocatalyst surface like a liquid film at this low temperature, so that an excess amount of CH₄ is required to perform PSRM (eqn (1)), but a further increase does not influence the CO selectivity as much. Moreover, one additional experiment was conducted in the flow of a gas mixture with a very high CH₄/H₂O ratio (90% CH₄ and 0.3% H_2O in Ar) at the flow rate of 15 ml min⁻¹ (Fig. S6[†]). The ratio of the consumed electrons and holes was not unity; $R(e^{-}/h^{+})$ was around 2. Since the CH₄ concentration was very high, it was suggested that methane decomposition occurs to form carbon although the reaction time was not long enough to change the color of the photocatalyst. However, these conditions gave a high CO selectivity of 39%, due to the further acceleration of the first PSRM (eqn (1)) and the limitation of the successive PWGS reaction (eqn (2)).

These results under various reaction conditions support the proposed scheme mentioned above (Scheme 1).

Conclusions

Photocatalytic steam reforming of methane (PSRM) to produce CO was successfully uncovered by employing a Ladoped NaTaO₃ photocatalyst without a cocatalyst. This reaction produces CO and CO₂ simultaneously. The presence of water and CO also initiates the photocatalytic water gas shift reaction (PWGS), which decreases the CO production rate. The selectivity to CO in the PSRM was controlled by the photocatalyst properties and the reaction conditions such as the light intensity, the flow rate of the reactant, and the ratio of CH₄ to H₂O in the feed gas mixture to some extent. However, an excellent achievement is very difficult to be obtained by changing these parameters in the present ranges with the current photocatalyst and the reaction system. Thus, the development of the photocatalyst and the reactor would be desirable for further improvement.

Author contributions

Wirya Sarwana: conceptualization, investigation, and writing – original draft. Akihiko Anzai and Daichi Takami: investigation. Akira Yamamoto: methodology and funding acquisition. Hisao Yoshida: conceptualization, funding acquisition, project administration, supervision, and writing – review & editing.

Conflicts of interest

There are no conflicts to declare.

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