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Effect of chloride ion as a hole scavenger on the photocatalytic conversion of \( \text{CO}_2 \) in an aqueous solution over Ni–Al layered double hydroxides

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Abstract

The photocatalytic conversion of CO\textsubscript{2} into useful chemical compounds in water without using organic sacrificial reagents is a promising method to overcome environmental and energy problems. Various synthesized layered double hydroxides (LDHs) are capable of reducing CO\textsubscript{2} to CO in an aqueous solution under UV light irradiation. However, it is difficult to oxidize H\textsubscript{2}O to O\textsubscript{2} in a photocatalytic system using LDHs as photocatalysts. In this study, we investigated the photocatalytic conversion of CO\textsubscript{2} using a Ni–Al LDH in an aqueous solution of NaCl. Hypochlorous acid (HClO) was produced as an oxidation product of Cl\textsuperscript{−} with the formation of reduction products such as CO and H\textsubscript{2} under photolysis. We propose the inclusion of Cl\textsuperscript{−} in the reaction solution to be one of the most promising ways for obtaining a hole scavenger, an approach that would enable the construction of an artificial photosynthesis system for the conversion of CO\textsubscript{2}.
Introduction

The use of photocatalytic reactions to convert CO$_2$ into valuable chemicals such as CO, HCHO, HCOOH, CH$_3$OH, and CH$_4$ is one of the most promising methods to develop a sustainable carbon cycling system. We previously reported the photocatalytic activity of ZrO$_2$, MgO, and Ga$_2$O$_3$, which have basic sites on their surface, for the conversion of CO$_2$ in the presence of H$_2$ as a reductant. This requires the conversion of CO$_2$ molecules, which are adsorbed on the surface of these photocatalysts, into active species to enable their facile reduction by the photogenerated electrons. Therefore, solid state basic materials are suitable candidates to construct photocatalytic systems required for the conversion of CO$_2$.

Layered double hydroxides (LDHs, [M$^{2+}$$_{1-3}$M$^{3+}$$_x$(OH)$_2$]$^{x+}$[A$_{x/2}$]$^{x-}$·$m$H$_2$O) are known as natural and/or synthetic clays that contain highly ordered two-dimensional hydroxide sheets. Their structures are based on edge-sharing octahedral units centred around a metal ion, which is coordinated to OH groups (M$^{2+}$$_6$(OH)$_6$), in which the divalent metal cations are partially substituted by trivalent metal cations. The LDH interlayer is known to be capable of retaining various kinds of anions to compensate for the positive charge of the hydroxide sheets. LDHs are widely used as basic materials for CO$_2$ capture and storage, removal of organic and inorganic anions from water, and base-catalysed reactions. We reported a series of synthetic M$^{2+}$−M$^{3+}$ LDHs (M$^{2+}$ = Mg, Ni, and Zn; M$^{3+}$ = Al, Ga, and In) that show activity toward the photocatalytic conversion of CO$_2$ in water. In particular, the use of Ni−Al layered double hydroxide (Ni−Al LDH) as a photocatalyst enabled us to achieve the maximum conversion of CO$_2$ to CO with high selectivity, because it produces lesser H$_2$ as a reduction product of H$^+$ derived from water than other LDHs. On the other hand, other LDHs such as Mg−In
LDH and Ni–In LDH, both of which contain In$^{3+}$ as a trivalent cation, increase the H$_2$ production, a less preferable result. This led us to conclude that Ni–Al LDHs offer suitable surface properties for the selective photocatalytic conversion of CO$_2$ in water. During previous research efforts, we used isotopic experiments to demonstrate that the CO$_2$ gas that was introduced as a substrate was indeed the origin of the CO evolved. Lately, LDHs have attracted considerable attention as photocatalysts for CO$_2$ conversion, water splitting using sacrificial reagents, and decomposition of organic compounds due to their environmentally friendly properties, characteristic layer structures, large specific surface areas, and remarkable adsorption capacities. Izumi et al., Katsumata et al., and Xu et al. have reported the photocatalytic conversion of CO$_2$ using synthetic LDHs.

Of late, many approaches to the overall photocatalytic water splitting reaction using reversible redox mediators such as I$_3^−$/I$^-\$28, IO$_3^-$/I$^-\$30, Fe$^{3+}$/Fe$^{2+}$32, 33, 34, and Co$^{3+}$/Co$^{2+}$35 have been explored. Matsumura et al. reported the reduction of H$_2$O to H$_2$ by using Br$^-$, which was oxidized to Br$_2$, and the oxidation of H$_2$O to O$_2$ using Fe$^{3+}$, which was reduced to Fe$^{2+}$ using a photoelectrochemical cell with two separate compartments. In their system, Br$_2$ (or Br$_3^-$) was produced as an oxidation product of Br$^-$ with the evolution of H$_2$. It is known that halide anions in photocatalytic systems can scavenge holes formed by the photoexcitation of electrons from the valence band to the conduction band of the photocatalysts. In this regard, both Krivec et al. and Pelizzetti et al. focused on the inhibition effects of Cl$^-$ during the photocatalytic degradation of organic compounds. Both these groups insisted that the Cl$^-$ that exists in the photocatalytic system can react with the photogenerated holes and consequently reduce the number of active oxidizing species capable of decomposing organic
molecules. However, the oxidation product of Cl$^-$ was not observed in either of these studies. In recent days, Li and co-workers reported that a small amount of Cl$^-$ in the reaction solution affected the photocatalytic activity for an overall water splitting to H$_2$ and O$_2$, through the photocatalytic oxidation of Cl$^-$ by the photogenerated holes $^{39}$. In this study, we attempted to detect the stoichiometric formation of the oxidation products of Cl$^-$ in the photocatalytic conversion of CO$_2$ using Ni–Al LDH in an aqueous solution of Cl$^-$, which was added as a hole scavenger.
Experimental Section

Catalyst preparation

Ni−Al LDHs with various Ni/Al ratios (Ni/Al = 2, 3, 4, and 5) were fabricated by using the typical coprecipitation method provided hereafter. A mixed aqueous solution of NiCl₂·6H₂O (Wako Pure Chemical Industries, Ltd., 99.9%) and AlCl₃ (Wako Pure Chemical Industries, Ltd., 98.0%) was slowly dropped into an aqueous solution of Na₂CO₃ (Wako Pure Chemical Industries, Ltd., 99.5%) at room temperature. The pH value was maintained between 9.9 and 10.1 by adding an aqueous solution of NaOH (Wako Pure Chemical Industries, Ltd., 97.0%) during the precipitation using a liquid feeding pump (NRP−76, NISSHIN RIKA, Japan) connected to a pH controller (NPH−660NDE, NISSHIN RIKA, Japan). The resulting suspension was transferred to a stainless steel autoclave equipped with an inner Teflon vessel, and aged under hydrothermal conditions at 383 K for periods ranging from 0 to 120 h. The solid precipitate was collected by filtration, washed with 1.0 L of ultra-pure water, and then dried at 383 K in air.

Catalyst characterization

The powder XRD patterns of the Ni−Al LDHs were measured by using an X-ray diffractometer (Ultime IV, Rigaku), using Cu Kα radiation (λ = 0.154 nm) at a scan speed of 4.0° min⁻¹. The Brunauer-Emmett-Teller (BET) specific surface area of the Ni−Al LDHs was estimated from their N₂ adsorption isotherms at 77 K using an adsorption analyser (BELSORP-miniII, BEL Japan, Inc.), prior to which each sample was evacuated at 383 K for 1 h using a pretreatment system (BELPREP-vacII, BEL Japan, Inc.). SEM images of Ni−Al LDHs were captured by using a Field Emission
Scanning Electron Microscope (FE-SEM, SU-8220, Hitachi High-Technologies) at the acceleration voltage of 3.0 kV. X-ray photoelectron spectroscopy (XPS) measurement of as-prepared Ni−Al LDH was performed by using an X-ray photoelectron spectrometer (ESCA 3400, Shimadzu Corp.). The Ni 2p spectra of Ni−Al LDH and reference samples were collected using Mg Kα X-ray source, and calibrated by the peak that can be assigned to C 1s absorption. Ni K-edge XAFS spectrum of Ni−Al LDH was measured at the BL01B1 of SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No. 2013A1615). The spectrum was recorded in a transmittance mode at room temperature, using Si(111) double crystal monochromator. The photon energy was calibrated by using Ni foil.

Photocatalytic activity test for the CO₂ conversion in an aqueous solution

The photocatalytic conversion of CO₂ was carried out in an aqueous solution by using a quartz inner-irradiation type reaction vessel in a quasi-flowing batch system. The photocatalyst powder was dispersed in 1.0 L of an aqueous solution, which was subsequently degassed using a stream of He gas. Following this, high purity CO₂ gas (99.999%) was bubbled into the aqueous solution containing the photocatalyst at a flow rate of 15 mL min⁻¹. The suspension was irradiated under a 400 W high-pressure mercury lamp via a quartz filter equipped with a cooling water system. The resulting products, namely CO, H₂, and O₂, were analysed by using a barrier discharge ionization detector gas chromatography (BID-GC) system using a gas chromatograph (GC-2010 Tracera, Shimadzu Corp.) equipped with a MICROPACKED ST column using He gas as a carrier. The selectivity toward CO evolution among the reduction products was given by Formula (1).
Formula (1)

\[
\text{Selectivity toward CO (\%) = } 100 \times \frac{(\text{CO} / \text{µmol})}{((\text{CO} / \text{µmol}) + (\text{H}_2 / \text{µmol}))}
\]

**DPD test**

The formation of hypochlorous acid (HClO) in aqueous solutions during the photocatalytic reactions can be confirmed by using a DPD method\(^4^0\)\(^4^1\), which is one of the most popular techniques to observe HClO in water, based on the oxidation potential of HClO. The most commonly used is a colorimetric method, based on addition of the \(N,N\)'-diethyl-\(p\)-phenylenediamine (DPD) reagent. If HClO is present in the sample solution, a red oxidized form of DPD yields rapidly through the stoichiometric reaction. The DPD solution was prepared by dissolving 0.06 g of the DPD reagent (Wako pure chemical, Japan), which is a mixture of DPD sulphate and \(\text{Na}_2\text{SO}_4\), in 3.0 mL of phosphate buffer solution (pH = 6.5). Following this, 1.0 mL of the prepared DPD solution was added to 5.0 mL of the sample solution, and was shaken for 20 s. The transmittance spectrum was measured immediately using a multiscan UV–vis spectrometer (MCPD-7700, Ohtsuka, Japan). The concentration of HClO in the aqueous solution was estimated from the absorbance at 515 nm.
Results and discussion

Figure 1(a–f) shows the XRD patterns of Ni–Al LDHs (Ni/Al = 4) aged under hydrothermal conditions at 383 K for various treating times (0–120 h). All the patterns corresponded to the typical structure of LDHs. The sharp diffraction peaks at 11.1° and 22.5°, which are marked with asterisks (*), can be assigned to the (003) and (006) phase reflections, respectively. The positions of these diffraction peaks depend on the size of the interlayer anions, i.e., the intercalation of large anions is responsible for the peak shift of these reflections. The XRD patterns revealed that the interlayer distance of Ni–Al LDH remained unchanged owing to aging under hydrothermal conditions, indicating that the anions that were present before the hydrothermal aging procedure are retained in the interlayer between the hydroxide sheets. In addition, the two diffraction peaks at around 60°, which are marked with daggers (†), can be attributed to the (110) and (113) phase, respectively. No change was observed in the position of these reflection peaks. Moreover, the broadened peaks between 30–40° might be caused by the (009) phase reflection overlapped with the (012) and (015) phases. The morphology of the as-synthesized Ni–Al LDH (Ni/Al = 4) was examined with scanning electron microscopy (SEM) as shown in Figure S1. It can be seen that many platelets are stacked according to the so-called the card-house type sheet aggregation. Table 1 lists the full width at half maximum of the (003) phase reflection (hereafter referred to as FWHM_{(003)}) and the specific surface area estimated from the N\textsubscript{2} adsorption isotherm using the BET method at liquid N\textsubscript{2} temperature (77 K). The FWHM_{(003)} was found to decrease gradually as the hydrothermal aging time was increased, indicating that stacking of the layer structure advanced in the direction of the c-axis owing to the hydrothermal treatment. Moreover, the specific surface area of Ni–Al LDH was also
found to depend on the aging time, and a maximum specific surface area was achieved after a hydrothermal aging treatment of 20 h. As reported by Jasra and coworkers, it is generally known that the crystallinity of hydrotalcite-like compounds is advanced by the hydrothermal treatment in accordance with the decrease in the specific surface area. The reason why the specific surface area of Ni–Al LDH was improved after hydrothermal treatment within 20 h is not clear, whereas the FWHM (003) monotonously decreased with the aging time. As shown in Figure 2, the Ni 2p XPS spectrum of as-synthesized Ni–Al LDH was almost the same as the spectra of Ni(OH)$_2$ and NiCO$_3$, and partially different from that of NiO. With reference to the previous reports, the binding energy (BE) value of the main Ni 2p$_{3/2}$ peak, at around 856.0 eV, was assigned to the Ni$^{2+}$ ion by comparison with the known BE value for the Ni 2p$_{3/2}$ photoelectrons of Ni(OH)$_2$. The Ni K-edge XANES spectrum of Ni–Al LDH which is shown in Figure S2, was not inconsistent with the result of the XPS measurement. The position of the absorption edge ($E_0$) and the intensity of the white line of Ni–Al LDH were very similar to those of Ni(OH)$_2$. It is indicated that the oxidation state and the coordination environment of Ni species in as-prepared Ni–Al LDH correspond to Ni(OH)$_2$; it is known that LDH group materials have a similar structure to the brucite (Mg(OH)$_2$) where octahedral of Mg$^{2+}$ (six-fold coordination to OH$^-$) share edges to form infinite sheets.

Figure 3(a) shows the formation rates of CO and H$_2$, both of which were reduction products of CO$_2$ dissolved in the solution and H$^+$ derived from H$_2$O, respectively, in the photocatalytic conversion of CO$_2$ in an aqueous solution of NaCl (0.1 M) using Ni–Al LDH (Ni/Al = 4) as a photocatalyst. The formation rate of CO after 1 h of photoirradiation was $1.7 \times 10^{-1}$ μmol min$^{-1}$, which was 3.4 times higher than that of H$_2$. 
No other reduction products of CO$_2$, such as formic acid, methane, and methanol, were obtained. Measurements confirmed that the oxidation of H$_2$O did not lead to the formation of any O$_2$ in our photocatalytic system. Meanwhile, the formation rates of CO and H$_2$ decreased during the first 10 h of photoirradiation, stabilizing at ca. 5.0×10$^{-2}$ μmol min$^{-1}$ and ca. 6.0×10$^{-3}$ μmol min$^{-1}$, respectively. Figure 3(b) shows the total amounts of the products, which were estimated from the formation rates through integration with time. The total amount of CO evolved as a reduction product of CO$_2$ increased with photoirradiation time and was 110.9 μmol after 29 h of photoirradiation. The structural changes in Ni–Al LDH through the photocatalytic reaction for 29 h were not observed in the XRD patterns that are shown in Figure S3. The value of FWHM(003) and the positions of the reflection peaks of Ni–Al LDH after the reaction were not changed as compared to those of as-synthesized one, indicating that the structural properties of Ni–Al LDH are not altered during the photocatalytic conversion of CO$_2$ in an aqueous solution of NaCl. As shown in Figure S4, on the other hand, the total amount of CO and H$_2$ evolved were gradually decreased with an increasing number of repetitions. This seems to indicate that the photocatalytic activity of the Ni–Al LDH photocatalyst is not as stable in our reaction system. Therefore, the cause of the changes in Ni–Al LDH during photoirradiation and how this might cause its deactivation for the photocatalytic conversion of CO$_2$ have not been clarified.

The effect of hydrothermal aging on the specific surface area of Ni–Al LDH (Ni/Al = 4), which is shown in Table 1, is represented again as a function of time in Figure 4. Ni–Al LDH (Ni/Al = 4), which was aged under hydrothermal conditions for a relatively short time, exhibited a larger specific surface area than when prepared without aging. The specific surface area of Ni–Al LDH (Ni/Al = 4) gradually decreased after
prolonged hydrothermal aging. This result is not inconsistent with the fact that extending the aging time causes Ni–Al LDH (Ni/Al = 4) to develop a high crystallinity in the direction of the $c$-axis, as shown in Table 1. On the other hand, Figure 4 also shows that the total amount of CO evolved from the photocatalytic conversion of CO$_2$ using Ni–Al LDH (Ni/Al = 4) is influenced by the aging time. The effect of the hydrothermal treating time on the change in the total amount of CO yielded after 8 h of photoirradiation was in good agreement with the specific surface area after the same length of hydrothermal treatment, indicating that the amount of CO evolved strongly depended on the magnitude of the surface area. In other words, Ni–Al LDH with a large specific surface area can achieve high photocatalytic activity for the conversion of CO$_2$ to CO, as shown in Figure S5. In contrast, the selectivity toward CO, which is given by Formula (1) in the experimental section, did not depend on the specific surface area, indicating that the selectivity is controlled by the surface properties corresponding to the Ni/Al ratio as described below. It should be noted that the adsorption of a CO$_2$ molecule on LDH is not a negligible step in the photocatalytic conversion of CO$_2$ in an aqueous solution, considering the results we previously published in this regard, which revealed that the introduced CO$_2$ molecules existed on the surface and/or in the interlayer of Ni–Al LDH, as was shown via a temperature-programmed desorption experiment using isotopic $^{13}$C-labeled CO$_2$ as a substrate.

**Figure 5** shows the total amounts of CO and H$_2$ evolved during the photocatalytic conversion of CO$_2$ in an aqueous solution of NaCl (0.1 M) using Ni–Al LDH with various Ni/Al ratios (Ni/Al = 2, 3, 4, and 5) after 8 h of photoirradiation. The total amounts of CO and H$_2$ evolved were influenced by the Ni/Al ratio of Ni–Al LDH, indicating that the selectivity toward CO evolution depended on the Ni/Al ratio. The
Ni–Al LDH with Ni/Al = 4 exhibited the highest conversion of CO₂ for the photocatalytic conversion of CO₂ using the various Ni/Al ratios. The Ni–Al LDH with Ni/Al = 5, which contains 83 mol% of nickel in the hydroxide sheet, showed a much higher activity for CO evolution and selectivity toward CO than Ni(OH)₂, indicating that the incorporation of Al³⁺ into Ni(OH)₂ to construct the LDH structure significantly enhanced the photocatalytic activity for the conversion of CO₂ in an aqueous solution.

In addition, Ni–Al LDHs (Ni/Al = 2, 3, 4, and 5) exhibited a higher selectivity to CO formation than Al(OH)₃ and Ni(OH)₂ as shown in Figure 5. Ebitani et al. demonstrated that the properties of basic sites of Mg–Al LDHs were changed as their Mg/Al ratio was changed ⁴⁸. It is suspected that the introduction of Al³⁺ into the Ni²⁺(OH)₆ octahedral unit affects the surface basicity, and that mixed hydroxides containing both Ni²⁺ and Al³⁺ in a certain ratio possess surface properties that are conducive to the photocatalytic conversion of CO₂.

It is well known that inorganic anions contained in a reaction solution are able to critically influence the photocatalytic activity. In 1992, Sayama and Arakawa demonstrated the effect of NaHCO₃ addition on the photocatalytic decomposition of H₂O and the photocatalytic reduction of CO₂ using ZrO₂ as a photocatalyst ⁴⁹. Recently, several researchers insisted that the addition of NaHCO₃ to the reaction solution is essential for achieving the photocatalytic conversion of CO₂ in water, because it improves the selectivity toward CO production ⁵⁰ ⁵¹. Table 2 presents the effect of the addition of anions to the reaction solution on the amounts of CO and H₂ evolved and the selectivity toward CO during the photocatalytic conversion of CO₂ in an aqueous solution using Ni–Al LDH (Ni/Al = 4) as a photocatalyst after 8 h of photoirradiation. The addition of NaHCO₃ or Na₂CO₃ promoted H₂ production via the reduction of H⁺
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derived from H₂O, whereas the amount of CO evolved was not affected by these additives. On the other hand, neither Na₂SO₄ nor NaNO₃ could positively affect product formation in our photocatalytic system. The presence of NaNO₃ led to the formation of O₂ under photoirradiation due to the photodecomposition of NO₃⁻. In contrast to the other inorganic salts, the addition of NaCl clearly enhanced the photocatalytic conversion of CO₂ to CO. The amount of CO evolved in a 0.1 M aqueous solution of NaCl after 8 h of photoirradiation was more than twice the amount that was found to evolve when pure water was used. Simultaneously, the addition of NaCl suppressed the formation of H₂ as a reduction product of H⁺. Accordingly, the selectivity toward CO evolution was advanced by the addition of NaCl to the reaction solution. Figure 6 shows the amounts of CO and H₂ evolved and the selectivity toward CO during the photocatalytic conversion of CO₂ in an aqueous solution containing various kinds of halogenides, using Ni−Al LDH as a photocatalyst after 5 h of photoirradiation. It can be seen that NaCl was no exception, and that other chloride salts such as KCl, CsCl, MgCl₂, and CaCl₂ influenced the selectivity toward CO evolution to a similar extent. This suggested that the presence of Cl⁻ in the reaction solution promoted the photocatalytic conversion of CO₂ regardless of the nature of the counter cations. However, the addition of iodide ions (I⁻) decreased the photocatalytic activity of the Ni−Al LDH for the evolution of CO and H₂. Abe et al. reported the overall water splitting system by using I⁻ as a redox mediator, which is oxidized by a hole generated by the photoexcitation of an electron from the valence band to the conduction band of a TaON photocatalyst under visible light irradiation. In our case, on the other hand, the colour change of the reaction solution to yellow during the reaction indicated that I⁻ might be converted into triiodine (I₃⁻) under UV light irradiation by capturing the photogenerated holes; hence,
the photocatalytic reaction over Ni−Al LDH was prevented by the presence of I$_3^-$ in the reaction suspension. We therefore propose Cl$^-$ in the reaction solution as one of the most promising candidates for a hole scavenger capable of functioning under UV light irradiation.

In addition, it is also necessary to discuss the stoichiometric formation of reduction and oxidation products for the photocatalytic conversion of CO$_2$. Iizuka et al. and Teramura et al. reported a photocatalytic system for the conversion of CO$_2$ with H$_2$O as a reducing reagent using ALa$_4$Ti$_4$O$_{15}$ (A = Ca, Sr, and Ba) and Zn-doped Ga$_2$O$_3$ photocatalysts, respectively, and determined that a stoichiometric amount of O$_2$ was evolved as an oxidation product of H$_2$O via the capturing of the photogenerated holes. In our system, in which Ni−Al LDH is used as a photocatalyst, however, O$_2$ was not formed at all during the photocatalytic reaction. Figure 7(a−h) shows the absorption spectra for the DPD test to confirm HClO in the reaction solution after the reaction for each photoirradiation time, which contains a certain amount of photocatalyst powder. Two intense absorption peaks around 515 nm and 555 nm were observed, and these peaks can be assigned to the oxidized form of DPD. In this study, the absorbance at 515 nm was used to estimate the concentration of HClO that was produced during the reaction as referred to in the previous report. The amount of HClO plotted versus the photoirradiation time is shown in Figure 7(i) with the amounts of reduction products such as CO and H$_2$. In the photocatalytic conversion of CO$_2$ using Ni−Al LDH (Ni/Al = 4) in an aqueous solution of NaCl (0.1 M), the products CO, H$_2$, and HClO were formed under photoirradiation as a reduction product of CO$_2$ and H$^+$, and as an oxidation product of Cl$^-$, respectively. It should be possible to detect HClO selectively by using a DPD (N,N-dimethyl-p-phenylenediamine) test due to the strong oxidation
power of HClO, i.e., the oxidation potentials of the other oxyanions of chlorine, ClO$_2^-$, ClO$_3^-$, and ClO$_4^-$, are insufficient to allow them to react with DPD. In the reaction solution, Cl$^-$ is considered to play the role of a reducing reagent and to be oxidized to HClO by the photogenerated holes during the photocatalytic reaction. Previous studies have attempted to use Cl$^-$ as a hole scavenger in a photocatalytic system; nevertheless, no oxidation product was observed for this anion. To the best of our knowledge, this is the first report to confirm the formation of HClO as an oxidation product of Cl$^-$ during a photocatalytic reaction. Figure 8 shows the influence of the NaCl concentration of the reaction solution on the total amounts of products formed after 8 h of photoirradiation. It can be seen that the total amounts of both the reduction (CO + H$_2$) and oxidation (HClO) products were affected by the NaCl concentration, and that the largest amount of these products was produced at a concentration of NaCl: 0.20 mol L$^{-1}$. The evolution of certain amounts of CO, H$_2$, and HClO in the absence of additional Cl$^-$ in the reaction solution was ascribed to the presence of residual Cl$^-$ on the Ni–Al LDHs. An elemental analysis revealed that more than 0.4 mmol g$^{-1}$ of Cl$^-$ derived from the precursors of the hydroxide sheets was contained in the Ni–Al LDHs, indicating that these Cl$^-$ ions might perform the same function as those in the reaction solution, in that they are partially oxidized to HClO. In this regard, one could speculate that Cl$^-$ is oxidized to chlorine (Cl$_2$) by capturing the photogenerated holes as shown in Formula (2), whereupon Cl$_2$ in the water would be expected to immediately undergo conversion to HClO and HCl via a disproportionation reaction (Formula (3)).

Formula (2) \[ 2\text{Cl}^- + 2\text{h}^+ \rightarrow \text{Cl}_2 \]
Formula (3) \[ \text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HClO} + \text{HCl} \]
Formula (4) \[ \text{CO}_2 + 2\text{H}^- + 2\text{e}^- \rightarrow \text{CO} + \text{H}_2\text{O} \]
Formula (5) \[ 2H^+ + 2e^- \rightarrow H_2 \]

Taking these reaction formulae into account, HClO could be regarded as a two-electron oxidation product of Cl\(^-\); thus, 2 \( \mu \text{mol} \) of holes should be consumed to form 1 \( \mu \text{mol} \) of HClO. Besides, it is known that CO and H\(_2\) are the two-electron reduction products of CO\(_2\) and H\(^+\), respectively (Formula (4) and (5)). An estimated ratio of the total number of consumed holes to electrons for 8 h of photoirradiation, plotted versus the concentration of NaCl, is shown in Figure 8. Below NaCl concentrations of 0.1 M, the value of the product ratio was approximately 1.0, indicating that the stoichiometric formation of reduction products and the oxidation product was achieved in this photocatalytic reaction. On the other hand, the ratio gradually decreased as the NaCl concentration increased. A high concentration of NaCl is considered to prevent the adsorption of HClO, which is produced during the reaction, on the surface of the Ni–Al LDH. HClO species that are not dissolved in the reaction solution, but are instead adsorbed on the surface of the Ni–Al LDH, can be detected by the DPD test, because HClO in an aqueous solution is known to be readily decomposed into HCl photochemically under UV light irradiation. Hence, the observed decrease in the ratio of the number of consumed holes to electrons may have been caused by the partial photodecomposition of HClO formed in the reaction solution at a high NaCl concentration. Accordingly, we concluded that stoichiometric amounts of CO and H\(_2\), as reduction products, and adsorbed HClO on Ni–Al LDH, as an oxidation product, evolved during the photocatalytic conversion of CO\(_2\) using Ni–Al LDH as a photocatalyst in an aqueous solution of 0.1 M NaCl under UV light irradiation.
Conclusion

The photocatalytic conversion of CO$_2$ in an aqueous solution was achieved by using synthetic Ni–Al LDH as a photocatalyst. After exposing the solution to photoirradiation for 29 h, the amount of CO (as a reduction product of CO$_2$) and the selectivity of the reduction products toward CO evolution were 110.9 μmol and 88.4%, respectively. The addition of Cl$^-$ to the reaction solution clearly improved the photocatalytic activity for the conversion of CO$_2$ to CO, and simultaneously suppressed the formation of H$_2$ as a reduction product of H$^+$. A DPD test revealed that, under photoirradiation, HClO is stoichiometrically formed as an oxidation product of Cl$^-$, together with reduction products such as CO and H$_2$. It is suggested that the Cl$^-$ present in the reaction solution functions as an effective hole scavenger and that it would be oxidized to Cl$_2$, which would immediately be converted into HClO in the presence of water.
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Table 1  Effect of the aging time under hydrothermal condition on the FWHM$_{(003)}$ and the specific area of Ni−Al LDH (Ni/Al =4). $^a$Aging: hydrothermal treatment at 383 K, $^b$full width at half maximum of (003) phase diffraction peak, $^c$specific surface area determined by N$_2$ adsorption isotherm.

<table>
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<tr>
<th>Aging$^a$ time / h</th>
<th>FWHM$_{(003)}$$^b$ / degree</th>
<th>SSA$^c$ / m$^2$ g$^{-1}$</th>
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</thead>
<tbody>
<tr>
<td>0</td>
<td>1.52</td>
<td>62.9</td>
</tr>
<tr>
<td>5</td>
<td>1.32</td>
<td>64.5</td>
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<tr>
<td>10</td>
<td>1.26</td>
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<td>1.23</td>
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<tr>
<td>60</td>
<td>1.17</td>
<td>94.3</td>
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<tr>
<td>90</td>
<td>1.08</td>
<td>61.1</td>
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<tr>
<td>120</td>
<td>1.07</td>
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</table>
Table 2  Effect of inorganic additives on the amounts of products evolved in the photocatalytic conversion of CO$_2$ in an aqueous solution using Ni–Al LDH (Ni/Al = 4). Concentration of additive: [anion] = 0.1 M, photocatalyst weight: 0.5 g, amount of solution: 1.0 L, CO$_2$ supply: 15 mL min$^{-1}$, light source: 400 W high-pressure Hg lamp, photoirradiation time: 8 h.

<table>
<thead>
<tr>
<th>Additive</th>
<th>Amount of products evolved</th>
<th>Selectivity to CO (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H$_2$ / μmol</td>
<td>CO / μmol</td>
</tr>
<tr>
<td>Non</td>
<td>21.0</td>
<td>25.2</td>
</tr>
<tr>
<td>NaHCO$_3$</td>
<td>83.6</td>
<td>21.8</td>
</tr>
<tr>
<td>Na$_2$CO$_3$</td>
<td>99.8</td>
<td>34.3</td>
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<tr>
<td>Na$_2$SO$_4$</td>
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<td>34.0</td>
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<tr>
<td>NaNO$_3$</td>
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<td>0.5</td>
</tr>
<tr>
<td>NaCl</td>
<td>9.3</td>
<td>56.4</td>
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</tbody>
</table>
Figure captions

Figure 1 XRD patterns of synthesized Ni–Al LDHs (Ni/Al = 4) via aging under hydrothermal condition at 383 K for (a) 0 h, (b) 5 h, (c) 10 h, (d) 20 h, (e) 60 h, and (f) 120 h.

Figure 2 Ni 2p XPS profiles of (i) NiO, (ii) NiCO$_3$, (iii) Ni(OH)$_2$, and (iv) synthesized Ni–Al LDH.

Figure 3 (a) Formation rates of CO (●) and H$_2$ (◇), and (b) total amounts of CO (●) and H$_2$ (◇) evolved in the photocatalytic conversion of CO$_2$ in an aqueous solution using Ni–Al LDH (Ni/Al = 4). Additive: 0.1 M NaCl, photocatalyst weight: 0.3 g, amount of solution: 1.0 L, CO$_2$ supply: 15 mL min$^{-1}$, light source: 400 W high-pressure Hg lamp.

Figure 3 Effect of the aging time under hydrothermal condition on the total amount of CO evolved in the photocatalytic conversion of CO$_2$ in an aqueous solution (left axis) after 8 h of photoirradiation and the specific surface area (right axis). Additive: 0.1 M NaCl, photocatalyst weight: 1.0 g, amount of solution: 1.0 L, CO$_2$ supply: 15 mL min$^{-1}$, light source: 400 W high-pressure Hg lamp.

Figure 5 Total amounts of products evolved and selectivity toward CO for the photocatalytic conversion of CO$_2$ in an aqueous solution using Al(OH)$_3$, Ni–Al LDH (Ni/Al = 2, 3, 4, and 5), and Ni(OH)$_2$. Black bar: CO, grey bar: H$_2$, circle: selectivity toward CO. Additive: 0.1 M NaCl, photocatalyst weight: 1.0 g, amount of solution: 1.0 L, CO$_2$ supply: 15 mL min$^{-1}$, light source: 400 W high-pressure Hg lamp, photoirradiation time: 8 h.

Figure 6 Total amounts of products evolved and selectivity toward CO for the photocatalytic conversion of CO$_2$ in an aqueous solution of various halogenide salts using Ni–Al LDH (Ni/Al = 4). Black bar: CO, grey bar: H$_2$, circle: selectivity toward
CO. Concentration of additive: [halide anion] = 0.1 M, photocatalyst weight: 0.5 g, amount of solution: 1.0 L, CO₂ supply: 15 mL min⁻¹, light source: 400 W high-pressure Hg lamp, photoirradiation time: 5 h.

**Figure 7** Absorption spectra for the DPD test to confirm HClO in the reaction solution after each photoirradiation time. (a) before the reaction and after the photoirradiation for (b) 1 h, (c) 2 h, (d) 3 h, (e) 4 h, (f) 5 h, (g) 6 h, and (h) 7 h. Sample solution including photocatalyst powder: 5.0 mL, DPD solution: 1.0 mL; (i) total amounts of products evolved for the photocatalytic conversion of CO₂ in an aqueous solution using Ni−Al LDH (Ni/Al = 4). White circle: H₂, grey circle: CO, black circle: total amounts of reduction products (H₂ + CO), black triangle: hypochlorous acid (HClO). Additive: 0.1 M NaCl, photocatalyst weight: 1.0 g, amount of solution: 1.0 L, CO₂ supply: 15 mL min⁻¹, light source: 400 W high-pressure Hg lamp.

**Figure 8** Influence of NaCl concentration on the photocatalytic conversion of CO₂ in an aqueous solution using Ni−Al LDH (Ni/Al = 4). Black circle: total amounts of reduction products (H₂ + CO), black triangle: amount of hypochlorous acid (HClO), white rhombus: ratio of oxidation product to reduction products. Additive: NaCl, photocatalyst weight: 1.0 g, amount of solution: 1.0 L, CO₂ supply: 15 mL min⁻¹, light source: 400 W high-pressure Hg lamp, photoirradiation time: 8 h.
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Figure 1(a−f)
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Figure 2
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![Graph showing formation rate vs. photoirradiation time]

**Figure 3(a)**
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![Figure 3(b)](image-url)
Figure 4
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Figure 5
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Figure 6
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![Absorbance spectrum](image)

Figure 7(a–h)
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Figure 7(i)

- Amount of products evolved / µmol
- Photoirradiation time / h

[Graph showing data points for different symbols and colors indicating changes over time]
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Figure 8

![Graph showing concentration of NaCl vs amount of products evolved (μmol) and oxidation product/reduction product ratio.](https://repository.kulib.kyoto-u.ac.jp)
Supporting Information

Figure S1   SEM image of synthesized Ni–Al LDHs (Ni/Al = 4) via aging under hydrothermal condition at 383 K for 20 h captured by using a Field Emission Scanning Electron Microscope (FE-SEM, SU-8220, Hitachi High-Technologies) at the acceleration voltage of 3.0 kV.
Figure S2   Ni K-edge XANES spectra of (a) Ni foil, (b) NiO, (c) Ni(OH)$_2$, and (d) as-prepared Ni–Al LDH. These spectra were measured at the BL01B1 of SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No. 2013A1615). The spectrum was recorded in a transmittance mode at room temperature, using Si(111) double crystal monochromator. The photon energy was calibrated by using Ni foil.
Figure S3  XRD patterns of Ni–Al LDHs (a) before and (b) after the photocatalytic reaction in an aqueous solution of NaCl.
Figure S4  The result of repeat test for the photocatalytic conversion of CO$_2$ in an aqueous solution of NaCl using Ni–Al LDH photocatalyst. CO: circle, H$_2$: diamond. Additive: 0.1 M NaCl, photocatalyst weight: 0.3 g, amount of solution: 1.0 L, CO$_2$ supply: 15 mL min$^{-1}$, light source: 400 W high-pressure Hg lamp.
Figure S5  Amount of CO evolved (circle) and selectivity toward CO (diamond) with the change of specific surface area of Ni–Al LDH photocatalyst in the photocatalytic conversion of CO\(_2\) in an aqueous solution of NaCl. Concentration of NaCl: 0.1 M, photocatalyst weight: 1.0 g, amount of solution: 1.0 L, CO\(_2\) supply: 15 mL min\(^{-1}\), light source: 400 W high-pressure Hg lamp, photoirradiation time: 8 h.