Photocatalytic conversion of CO₂ in water over Ag- modified La₂Ti₂O₇

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Abstract

We have found that Ag-modified La₂Ti₂O₇ with a layered perovskite structure exhibits activity for the photocatalytic conversion of CO₂ to CO in pure water. The evolution of O₂ proves that H₂O works as an electron donor for the photocatalytic conversion of CO₂. CO was generated as the main product, and CO, H₂, and O₂ were produced in stoichiometric amounts. The crystallite size of La₂Ti₂O₇ increased and the surface area decreased with increasing calcination temperature and time. Maximization of the photocatalytic activity of La₂Ti₂O₇ was accomplished by making a trade-off between the crystallite size and surface area. In addition, the loading amount and modification method of the Ag cocatalyst also influenced the amount of CO evolved. An isotope labeling experiment using ¹³CO₂ confirmed that the origin of evolved CO was not the residual carbon species on the La₂Ti₂O₇ surface, but was rather the CO₂ gas that was introduced during the experimental process.

Keywords: Conversion of CO₂ to CO, La₂Ti₂O₇ photocatalyst, Evolution of O₂, Isotope labeling.

Introduction

Due to the increased rates of deforestation and combustion of fossil fuels, CO₂ greenhouse gas emissions in the atmosphere is increasingly becoming an environmental hazard due to an accelerated rise in global temperatures [1,2]. Therefore, it is essential to not only control the level of CO₂ emissions, but to devise strategies to effectively remove CO₂ from the atmosphere. Among the various strategies for reducing the concentration of CO₂, the catalytic conversion of CO₂ to liquid fuels and chemicals is appealing due to the utilization of CO₂ as a natural derivative for production [3,4]. However, elevated temperature-pressure processes require a significant input of energy. Using solar light as an ideal and abundant energy source, it is possible to devise a promising route for the photocatalytic conversion of CO₂ into useful chemical products such as CO, HCOOH, HCHO, CH₃OH, and CH₄ under ambient temperature and pressure conditions [5,6].

The photocatalytic conversion of CO₂, an example of artificial photosynthesis, is a thermodynamically uphill reaction that utilizes photo-generated electrons as a source of energy [7]. It is difficult to achieve the reduction of CO₂ by H₂O over heterogeneous photocatalysts due to the competing generation of H₂ gas from the overall splitting of water [8]. Moreover, a stoichiometric amount of evolved O₂ should also be obtained if H₂O functions as an electron donor during the photocatalytic conversion of CO₂. Although various photocatalysts such as TiO₂ [9,10], CdS [11], BiVO₄ [12], and ZnGa₂O₄ [13] have been reported for the reduction of CO₂ in H₂O, the evolution of O₂ was not observed in the reaction, implying that the consumption of photogenerated holes is ambiguous. Until recently, Kudo et al. have discovered the photocatalytic conversion of CO₂ by H₂O over Ag modified ALa₄Ti₄O₁₅ (A=Ca, Sr, and Ba), where the amount of evolved CO was higher than the amount of evolved H₂, and a stoichiometric amount of O₂ was also simultaneously observed [14].

It is known that La-Ti based oxide materials with a layered perovskite structure can efficiently decompose H₂O into H₂ and O₂ without any sacrificial reagents under UV light irradiation [15-18]. Among La-Ti oxides, La₂Ti₂O₇, which possesses a (110) plane-type perovskite structure, was reported to show good photocatalytic activity for

overall water splitting [15,16,18]. Since the reduction of CO₂ requires a reduction potential higher than that for H⁺, the wide bandgap of La₂Ti₂O₇, which is capable of generating photoelectrons with a high reduction potential, should result in the efficient reduction of CO₂. In order to obtain a high crystallinity and surface area at low calcination temperature, we used a polymerized complex method over the typical solid state reaction method to prepare La₂Ti₂O₇ [15,18]. In this study, La₂Ti₂O₇ was fabricated using the polymerized complex method, and the photocatalytic conversion of CO₂ by H₂O over Ag-modified La₂Ti₂O₇ was investigated.

Experimental section

La₂Ti₂O₇ was fabricated using a polymerized complex method, where a defined amount of titanium tetraisopropoxide (Ti[OCH(CH₃)₂]₄, 95.0%, Wako) was dissolved in 0.2 mol of ethylene glycol (C₂H₆O₂, 99.5%, Wako) at room temperature. 0.3 mol of anhydrous citric acid (C₆H₈O₇, 98.0%, Wako) was then added and the mixture was heated with continuous stirring at 333 K. After the complete dissolution of citric acid, an appropriate amount of lanthanum nitrate (La(NO₃)₃·6H₂O, 99.9%, Wako) and 20 mL of methanol were added into the above solution. The additive ratio between La(NO₃)₃ and Ti[OCH(CH₃)₂]₄ was 1:1. The mixture was heated at 403 K for 3 h to obtain a transparent gel without any precipitated solid. The viscous gel was pyrolyzed at 623 K to remove all carbon-containing compounds, and the resulting powder precursor was calcined from 1173 to 1423 K for 1–8 h in static air. The Ag cocatalyst was chemically modified on La₂Ti₂O₇ through a series of chemical reduction, impregnation, and photodeposition methods. In the chemical reduction method, an aqueous NaPH₂O₂ solution was added into 100 mL of a suspension of photocatalysts (2.0 g) containing AgNO₃. After stirring at 333 K for 2 h, the modified photocatalyst was washed with deionized water three times and dried under vacuum at room temperature. In the impregnation method, photocatalysts were homogeneously dispersed in an aqueous AgNO₃ solution. The solution was then evaporated, dried, and calcinated at 723 K in a stream of dry air for 2 h. The photodeposition method was employed in situ during the photocatalytic conversion of CO₂. The structure and crystallinity of La₂Ti₂O₇ samples were characterized by X-ray diffraction (XRD) using a Rigaku Multi Flex powder X-

ray diffractometer. The UV-Vis diffused reflectance spectra (UV-Vis DRS) were measured by a JASCO Corporation V-670 spectrometer equipped with an integrating sphere. Spectralon[®], supplied by Labsphere Inc., was used as a standard reflection sample. The Brunauer–Emmett–Teller (BET) surface area was measured by N₂ adsorption at 77 K using a volumetric gas adsorption apparatus (BELmini, Bel Japan, Inc.). The Ag K-edge (25.5 keV) X-ray absorption fine structure (XAFS) measurements were made in the fluorescence mode at the BL01B1 beamline of the SPring-8 synchrotron radiation facility (Hyogo, Japan). The spectra were reduced by a Rigaku REX2000 program Ver. 2.5.9 (Rigaku Corp.). **TEM images were obtained with a JEOL JEM-1400 transmission electron microscope (TEM) operating at an accelerating voltage of 120 kV.**

The photocatalytic reaction was carried out in a flow system using an inner-irradiation-type reaction vessel at room temperature and ambient pressure. The photocatalyst (1.0 g) was dispersed in ultra-pure water (1.0 L), and CO₂ (99.999%) was bubbled into the water at a flow rate of 30 mL min⁻¹. The suspension was irradiated under a 400 W high-pressure mercury lamp with a quartz filter connected to a cooling water system. Generated gaseous products such as H₂, O₂, and CO were analyzed by thermal conductivity detector-gas chromatography (TCD-GC) using a GC-8A chromatograph (Shimadzu Corp.) equipped with a Molecular Sieve 5A column, (carrier gas: Ar) and by flame ionization detector-gas chromatography (FID-GC) using a methanizer and a Shincarbon ST column (carrier gas: N₂). In the isotope labeling reaction using ¹³CO₂, an inner-irradiation-type reaction vessel was connected to a closed circulating system with a vacuum line. The prepared Ag-modified La₂Ti₂O₇ sample (500 mg) was dispersed in ultrapure water (350 mL). ¹³CO₂ (2000 mmol), which was purified by vacuum distillation at liquid-N₂ temperature, was introduced into the reactor, and the suspension was irradiated by a 400 W high-pressure mercury lamp through a quartz filter connected to a cooling water system. The formation of either ¹³CO or ¹²CO after 5.5 h was analyzed by a quadrupole-type mass spectrometer (BEL Japan, Inc., BEL Mass) combined with a TCD-GC (Carrier gas: Ar).

Results and Discussion

Figure 1 shows the XRD patterns of La₂Ti₂O₇, which was prepared using the polymerized complex method with subsequent calcination at 1373 K for 4 h. In accordance with the standard pattern (ICSD#1950), La₂Ti₂O₇ exhibits a layered perovskite structure, which consists of perovskite-like slabs with a thickness equivalent to four corner-linked (TiO₆) octahedra. The edge of the TiO₆ octahedra is exposed to the interlayers of La₂Ti₂O₇, which run parallel to the (110) plane of the bulk perovskite slabs to give a (110) plane-type perovskite structure [18]. Figure 2 shows the UV–Vis DRS of La₂Ti₂O₇ after conversion of the reflection coefficient, R , to the absorption coefficient, $F(R_{\infty})$, through the Kubelka–Munk function, $F(R_{\infty}) = (1 - R^2)/2R$. The bandgap energy was derived from Davis–Mott’s equation, $\alpha h\nu = (h\nu - E_g)^n$, where α is the absorption coefficient; $h\nu$ is the energy of the irradiated light; and E_g is the bandgap energy. n is an experimental value, where the values for indirect allowed, indirect forbidden, direct allowed, and direct forbidden transitions are 2, 3, 1/2, and 3/2, respectively [19]. As shown in the inset of Figure 2, this equation ($n = 1/2$, direct allowed transition), gives an estimated value of 4.05 eV for the bandgap energy of La₂Ti₂O₇.

Figure 3a shows XRD patterns of a sample of La₂Ti₂O₇ that was treated at temperatures ranging from 1173 K to 1423 K. All samples exhibited the layered perovskite structure of La₂Ti₂O₇ without any impurity phases, which indicates that calcination above 1173 K following the polymerized complex procedure successfully caused crystallization of La₂Ti₂O₇. It has already been reported that crystalline La₂Ti₂O₇ was obtained by calcination above 1173 K, and that the photocatalytic activity of La₂Ti₂O₇ calcined below 1173 K was almost negligible [18]. In addition, all the peaks in the XRD patterns of La₂Ti₂O₇ became sharper and higher with an increase in the calcination temperature. The crystallite size of La₂Ti₂O₇ could be obtained using the FWHM (Full Width of Half Maximum) of XRD peaks, based on Scherrer’s equation. As shown in Figure 3b, the crystallite size of La₂Ti₂O₇ calcined at temperatures ranging from 1173 K to 1423 K increased linearly from 34.0 nm to 50.8 nm. On the other hand, the specific surface area of La₂Ti₂O₇, measured by the BET method, decreased when the calcination temperature was elevated (Figure 3b). These results mean that calcination at

various high temperatures affects not only the crystallite size, but also the specific surface area of La₂Ti₂O₇. Since photocatalytic activity is dependent on the crystallinity and surface area of the photocatalyst, the activities of La₂Ti₂O₇ calcined at various temperatures were monitored to compare the photocatalytic conversion of CO₂ by H₂O under UV irradiation. All the samples were modified with Ag using the chemical reduction method. Figure 3c shows the amount of CO, O₂, and H₂ evolved in 7 h. CO was evolved as the main reduction product, and a significantly smaller yield of evolved H₂ was observed. The simultaneous evolution of O₂ indicated that H₂O worked as an electron donor to consume the holes generated during the photocatalytic conversion of CO₂. Increasing the calcination temperature of La₂Ti₂O₇ from 1173 K to 1373 K caused an increase in the activity for the photocatalytic conversion of CO₂. This can be attributed to the high crystallinity of La₂Ti₂O₇ in spite of the decrease in the specific surface area. The maximum amount of CO evolved was observed over La₂Ti₂O₇ calcined at 1373 K. However, the activity of La₂Ti₂O₇ declined upon calcination at temperatures higher than 1373 K.

The calcination time also influences the crystallinity and surface area of La₂Ti₂O₇. As shown in Figure 4a, La₂Ti₂O₇ samples that were calcined at 1373 K for 1 to 8 h experienced an increase in peak intensities in the XRD pattern for each sample. The crystallinity of La₂Ti₂O₇ grew with longer calcination times, whereas the BET surface area was reduced (Figure 4b). As seen with varied calcination temperature, changes in calcination time from 1 h to 8 h also influence the activity of La₂Ti₂O₇. La₂Ti₂O₇ that was calcined at 1373 K for 4 h possessed a crystallite size of 47.3 nm and a specific surface area of 5.5 m² g⁻¹ to afford the highest activity for the photocatalytic conversion of CO₂ by H₂O. Generally, a high specific surface area and crystallinity are essential for an efficient heterogeneous photocatalyst. This is because the photocatalytic reaction occurs mostly on the surface of the photocatalyst, and the high crystallinity of the photocatalyst allows a smooth charge separation. Unfortunately, fabrication conditions such as calcination temperature and time can only promote high crystallization of the photocatalyst at the expense of a diminished surface area. This inverse relationship needs to be fine-tuned in order to maximize photocatalytic activity.

In the electrochemical reduction of CO₂, it has been proven that metallic Ag functions as an effective electrode for the conversion of CO₂ to CO [20]. In the case of the photocatalytic conversion of CO₂ by H₂O, the introduction of an Ag cocatalyst plays an important role in generating CO. In comparison with impregnation and in-situ photo deposition methods, Figure 5 shows that Ag species prepared by the chemical reduction method significantly enhanced the photocatalytic activity for the conversion of CO₂ to CO. This result indicates that the structure of the Ag cocatalyst on the surface of La₂Ti₂O₇ is highly dependent on the modification method. The UV-Vis DRS of Ag-modified La₂Ti₂O₇ loaded by various methods (Figure S1) showed the same intrinsic absorption as that of bare La₂Ti₂O₇. Different surface plasmon absorption in the visible and near-infrared region could be observed for the three samples due to the different particle size and dispersion of Ag cocatalysts. [14,21] The Ag-K edge XANES and Fourier-transformed Ag K-edge EXAFS spectra of Ag-modified La₂Ti₂O₇ prepared by the three methods are shown in Figure 6, of which Ag foil and Ag₂O were used as references. The similar XANES spectra of the three samples and Ag foil clearly proves that Ag species modified by the three methods are metallic Ag. This means the photocatalytic activity is not affected by the chemical state of Ag cocatalyst. Otherwise the Ag-Ag shell intensity of Ag species prepared by the chemical reduction method is much lower than those of Ag species fabricated by the impregnation and photodeposition methods in the FT of EXAFS spectra, which indicates the particle size of Ag cocatalysts in the chemical reduction sample is the smallest among the three samples. Figure 7 represents TEM images of Ag-modified La₂Ti₂O₇ loaded by the three methods. Actually, Ag nanoparticles prepared by the chemical reduction method are highly dispersed on the surface of La₂Ti₂O₇ with the particle size between 2 and 10 nm. In contrast, the wet impregnation and photodeposition methods result in the aggregation of Ag particles and poor Ag dispersion on La₂Ti₂O₇. It is noted that the formation of metallic Ag nanoparticles with the small size and uniform distribution by the chemical reduction method caused the enhancement for the photocatalytic conversion of CO₂ in water.

Table 1 shows the photocatalytic activity of Ag-modified La₂Ti₂O₇ prepared by the chemical reduction method with various loading amounts of Ag. While conversion

of CO₂ could occur on bare La₂Ti₂O₇, the evolution rate of H₂ (2.7 μmol h⁻¹) was higher than that of CO (0.8 μmol h⁻¹). This is because conversion of CO₂ competes with the splitting of water at an insufficient number of suitable reaction sites on bare La₂Ti₂O₇. Modification of La₂Ti₂O₇ with an Ag cocatalyst caused a dramatic increase in the photocatalytic activity for CO evolution. While the evolution rate of CO increased with the addition of larger amounts of Ag ranging from 0 to 1.0 wt%, the rate declined with higher amounts of Ag. The maximum activity was obtained for La₂Ti₂O₇ with 1 wt% of the Ag cocatalyst. It is clear that the modification by the Ag cocatalyst provided enough catalytic sites for the reduction of CO₂ on the surface of La₂Ti₂O₇, and the conversion of CO₂ to CO took precedence over H₂ production at such sites. In addition, the evolution of H₂ was also improved through the introduction of the Ag cocatalyst, possibly owing to the promotion of electron-hole separation. The Ag cocatalyst efficiently captures the photogenerated electrons and supplies them for the reductions of both CO₂ and H⁺. Any remaining photogenerated holes are consumed by the oxidation of H₂O to produce a stoichiometric amount of O₂. The equivalence between the reacted electrons and holes confirms that a perfect redox reaction occurred on the surface of Ag-modified La₂Ti₂O₇.

Figure 8 shows the time course of CO, H₂, and O₂ evolution during the photocatalytic conversion of CO₂ by H₂O over Ag-modified La₂Ti₂O₇ under optimized conditions. The evolution rates of CO, H₂, and O₂ at the steady state (5.2, 4.9 and 5.3 μmol h⁻¹, respectively) are in a stoichiometric ratio, indicating that CO₂ is efficiently reduced by H₂O over the Ag-modified La₂Ti₂O₇ photocatalyst, and that H₂O is simultaneously oxidized by the generated holes. In addition, CO was produced in priority to H₂. After 7 h, the amount of evolved CO was 47.7 μmol, which was higher than the amount of evolved H₂ (36.4 μmol). It can be observed that the formation rate of CO declined gradually at the initial stage of the reaction. Figure 9 shows the Ag K-edge XANES and Fourier-transformed Ag K-edge EXAFS spectra of Ag-modified La₂Ti₂O₇ before and after the photocatalytic reaction using Ag foil and Ag₂O as references. The XANES spectra of the Ag-modified La₂Ti₂O₇ before and after the reactions were similar to that of Ag foil, implying that the Ag species remained as metallic Ag after the photocatalytic reaction. In the corresponding EXAFS spectra, the height of the Ag-Ag shell peak increased after the photocatalytic reaction, indicating that the particle size of

the Ag cocatalyst on the surface of La₂Ti₂O₇ became larger after the reaction. Moreover, the grown Ag particles after the reaction can be distinctly observed in TEM images as shown in Figure S2. The change in the Ag particle size is attributed to the redeposition and aggregation of Ag species on the photocatalyst during photoirradiation [14]. This decreased the rate of formation of CO during the initial stage. After 3 h of photoirradiation, the rate became constant. On the other hand, the amount of evolved H₂ and O₂ increased linearly over 7 h of photoirradiation. This means that Ag-modified La₂Ti₂O₇ is a very stable photocatalyst for the photocatalytic conversion of CO₂ by H₂O, and is not affected by the oxidation and reduction of the generated hole and electron. The XRD patterns of fresh and recycled Ag-modified La₂Ti₂O₇ (Figure 10) clarified that the crystalline structure of La₂Ti₂O₇ after the photocatalytic reaction was almost the same as that before the photocatalytic reaction. The La₂Ti₂O₇ photocatalyst prepared by the polymerized complex method is very stable under UV light irradiation and in aqueous medium.

The La₂Ti₂O₇ photocatalyst was calcined at high temperatures in air during the fabrication process; this high-temperature treatment eliminates any carbon residues on the photocatalyst surface. However, it is necessary to confirm the carbon source of the gaseous products such as CO through an isotope-labeling reaction using ¹³CO to avoid any misestimations in the photocatalytic conversion of CO₂. Figure 11 displays the mass spectra (m/z 28 and 29) during the photocatalytic conversion of ¹³CO₂ by H₂O over Ag-modified La₂Ti₂O₇ under optimized conditions. Sampling gas was introduced into the mass spectrometer after it was segregated by a gas chromatograph. The peak in the spectrum at m/z = 29, which appeared at the same retention time as that observed by GC, can be directly attributed to ¹³CO gas. The amount of ¹³CO estimated by mass spectrometry was almost consistent with the amount of CO determined by TCD-GC. This result revealed that the evolution of CO was not from the contamination of La₂Ti₂O₇, but from the introduced CO₂ gas.

Conclusions

Ag-modified La₂Ti₂O₇ exhibited activity for the photocatalytic conversion of CO₂ to CO together with the oxidization of H₂O to O₂. H₂O functions as an efficient

electron donor for the reduction of CO₂, and the stoichiometric amounts of evolved CO, H₂, and O₂ indicate that the number of electrons used for the evolution of CO and H₂ is equal to the number of holes consumed for the evolution of O₂. The photocatalytic activity depends on the crystallinity and surface area of La₂Ti₂O₇, which are influenced by the calcination temperature and time. Thus, the maximum amount of CO was produced over La₂Ti₂O₇ that was synthesized using the polymerized complex method and calcined at 1373 K for 4 h. The isotope labeling reaction using ¹³CO₂ provided evidence that the evolved CO did not originate from carbon contamination of La₂Ti₂O₇, but from experimentally introduced CO₂ gas.

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Table 1 Effect of Ag content on the photocatalytic conversion of CO₂. La₂Ti₂O₇ was calcined at 1373 K for 4 h. Ag cocatalyst was modified by chemical reduction method.

Loading amount	Activity ($\mu\text{mol h}^{-1}$)			Reacted electrons ($\mu\text{mol h}^{-1}$)	Reacted holes ($\mu\text{mol h}^{-1}$)
	H ₂	O ₂	CO		
0 wt%	2.7	2.3	0.8	7.0	9.2
0.5wt%	4.9	5.2	4.6	19	21
1.0wt%	4.9	5.3	5.2	20	21
1.5wt%	4.3	4.8	4.3	17	19
2.0wt%	3.9	4.4	4.1	16	18

Figure captions

- Figure 1 XRD patterns of La₂Ti₂O₇ fabricated by polymerized complex method with calcination at 1373 K for 4 h.
- Figure 2 UV-vis DRS of La₂Ti₂O₇ prepared by polymerized complex method with calcination at 1373 K for 4 h. Inset: The plots of $(\alpha h\nu)^2$ versus the energy of light ($h\nu$) afford the band gap energy for La₂Ti₂O₇.
- Figure 3 (a) XRD patterns of La₂Ti₂O₇ at various calcination temperature; (b) Crystallite size and specific surface area of La₂Ti₂O₇ at various calcination temperature; (c) Evolution of CO (circle), O₂ (square), and H₂ (triangle) in 7 h over La₂Ti₂O₇ calcined at various temperature for 4 h. Ag cocatalyst was modified by chemical reduction method and the loading amount was 1 wt%.
- Figure 4 (a) XRD patterns of La₂Ti₂O₇ calcined at 1373 K for different time; (b) Crystallite size and specific surface area of La₂Ti₂O₇ calcined at 1373 K for different time; (c) Evolution of CO (circle), O₂ (square), and H₂ (triangle) in 7 h over La₂Ti₂O₇ calcined at 1373 K for different time. Ag cocatalyst was modified by chemical reduction method and the loading amount was 1 wt%.
- Figure 5 Amount of evolved gases for the photocatalytic reduction of CO₂ in 7 h over Ag-modified La₂Ti₂O₇ prepared by CR (chemical reduction method), PD (photodeposition method), and IMP (impregnation method). La₂Ti₂O₇ was calcined at 1373 K for 4 h and the loading amount of Ag was 1 wt%.
- Figure 6 Ag K-edge XANES (a) and Fourier transformed EXAFS (b) spectra of the Ag-modified La₂Ti₂O₇ prepared by chemical reduction method (red), photodeposition method (blue), impregnation method (green). Ag foil (black) and Ag₂O (purple) were references. La₂Ti₂O₇ was calcined at 1373 K for 4 h and the loading amount of Ag was 1 wt%.
- Figure 7 TEM images of Ag-modified La₂Ti₂O₇ prepared by chemical reduction (a), photodeposition (b), and impregnation (c) methods. La₂Ti₂O₇ was calcined at 1373 K for 4 h and the loading amount of Ag was 1 wt%.

- Figure 8 Time courses of CO (circle), O₂ (square), and H₂ (triangle) evolved for the photocatalytic conversion of CO₂ in water over Ag-modified La₂Ti₂O₇. La₂Ti₂O₇ was calcined at 1373 K for 4 h. Ag cocatalyst was modified by chemical reduction method and the loading amount was 1 wt%.
- Figure 9 Ag K-edge XANES (a) and Fourier transformed EXAFS (b) spectra of the optimized Ag-modified La₂Ti₂O₇ before (red) and after (blue) the photocatalytic conversion of CO₂. Ag foil (black) and Ag₂O (purple) were references. La₂Ti₂O₇ was calcined at 1373 K for 4 h. Ag cocatalyst was modified by chemical reduction method and the loading amount was 1 wt%.
- Figure 10 XRD patterns of La₂Ti₂O₇ (a) before and (b) after the reaction. La₂Ti₂O₇ was synthesized by polymerized complex method and calcined at 1373 K for 4 h. Ag cocatalyst was modified by chemical reduction method and the loading amount was 1 wt%.
- Figure 11 Mass spectra (m/z 28 and 29) after 5.5 h of photoirradiation in the photocatalytic conversion of ¹³CO₂ in water over Ag-modified La₂Ti₂O₇. La₂Ti₂O₇ was calcined at 1373 K for 4 h. Ag cocatalyst was modified by chemical reduction method and the loading amount was 1 wt%.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11