**Supplementary Information**

**Enhanced CO Evolution for Photocatalytic Conversion of CO2 by H2O over** **Ca Modified Ga2O3**

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**Supplementary Methods**

**Preparation of photocatalysts electrodes**

Ga2O3 and Ga2O3\_Ca photocatalysts electrodes were prepared on a fluorine doped tin oxide (FTO) glass via an electrophoresis deposition method. 100 mg of photocatalyst powder was added into 50 mL of an acetone solution containing 10 mg of iodine as an electrolyte, and then the photocatalyst powder was dispersed thoroughly by an ultrasonication. Prior to use, FTO glass (AGC fabritech Co., Ltd) was washed with aceton and 2-propanol solution in turn. Two FTO glasses were immersed in the solution with facing each other, and direct current (DC) was applied between the two FTO glasses by using an electrochemical measurement system (HZ-5000, Hokuto Denko Corp.), at 0.1 mA stable current (2 min) for measurements in an aqueous solution, and at 10.0 V stable voltage (5 min) for those in an organic solution. After drying at room temperature in air, prepared photocatalyst electrode was heated at 473 K for 2 h in order to remove the residual iodine.

**Electrochemical impedance measurements**

Electrochemical impedance measurements were performed using a three-electrode electrochemical cell consisting of the prepared photocatalyst/FTO electrode, Ag/AgCl electrode, and Pt wire as working electrode, reference electrode, and counter electrode, respectively. Prior to the measurements, the dissolved air in the electrolyte solution was completely removed by N2 gas flow. An aqueous Na2SO4 solution (0.1 M) was used as an electrolyte solution. The imaginary component of the impedance (Z’’) of the equivalent circuit including photocatalyst/FTO electrode was evaluated at an alternating current frequency of 39.8, 31.6, and 25.1 kHz with a sweeping applied voltage from 0.5 to −0.5 V vs. Ag/AgCl by an electrochemical measurement system (HZ-5000, Hokuto Denko Corp.). The capacitance (***C***) of the circuit was calculated from the imaginary component of the impedance (***Z*’’**) using the relationship,

│***Z*’’**│ = 1/(2**π*fC***) Eq. S1

where **π**and ***f*** means the circumference ratio and the frequency of the alternating current. The value of the flat band potential (hereinafter “***EFB***”) for the working electrode was estimated by using the resulted value of ***C*** in accordance with Mott-Schottky equation,

***C***−2 = (2/***εε*ₒ*A***2***eN*D**) (***E***−***E*FB**−***k*B*T***/***e***) Eq. S2

where: ***C*** and ***A*** are the interfacial capacitance and area, respectively, ***N*D** the number of donors, ***E*** the applied potential, ***k*B** Boltzmann’s constant, ***T*** the absolute temperature, ***ε*** the dielectric constant of the semiconductor, ***ε*ₒ** the permittivity of free space, and ***e*** is the electronic charge. Therefore, the value of ***E*FB**should be obtained from the intercept on *x*-axis in the plot of ***C***−2 versus the applied potential ***E***.

**The conversion rate of CO2 into CO:**

Flowing rate of CO2 = 30 mL min−1

Formation rate of CO = 835 µmol h−1

The concentration of CO in 30 mL min−1 of CO2 = *V*co/*V*CO2 = (835 × 10−6 × 8.31 × 103 × 303/ (1.013 × 105))/(30 × 60 × 10−3) × 106= 11531 ppm

The conversion rate of CO2 to CO = 1.15% ≈ 1.2%

**Supplementary Table 1.** Summary of photocatalysts for the conversion of CO2 into CO using H2O as an electron donor under similar experimental conditions.

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Catalyst** | **Weight/g** | **Light source** | **Co-catalyst** | **Additive** | **Activity / μmol h−1** | | | **Selec. to CO**/**%** | **Ref.** |
| **H2** | **O2** | **CO** |
| BaLa4Ti4O15 | 0.3 | 400-W Hg lamp | 2.0 wt%  Ag | None | 10.0 | 16.0 | 22.0 | 68.8 | 1 |
| NaTaO3:Ba | 1.0 | 400-W Hg lamp | 3.0 wt%  Ag | 0.1 M  NaHCO3 | 31.0 | 170a | 318 | 91.0 | 2 |
| CaTiO3 | 0.3 | 100 W Hg lamp | 3.5 wt%  Ag | 1.0 M  NaHCO3 | 3.10 | 25.0 | 54.0 | 94.0 | 3 |
| Na2Ti6O13 | 0.2 | 100 W Hg lamp | 1.0 wt%  Ag | 0.5 M  NaHCO3 | 1.60 | 0.70a | 4.60 | 74.0 | 4 |
| La2Ti2O7 | 1.0 | 400-W Hg lamp | 1.0 wt%  Ag | 0.1 M  NaHCO3 | 4.09 | 5.30 | 5.20 | 51.5 | 5 |
| ZnGa2O4 | 1.0 | 400-W Hg lamp | 1.0 wt%  Ag | 0.1 M  NaHCO3 | 8.50 | 74.3 | 155 | 95.0 | 6 |
| ZnGa2O4/  Ga2O3 | 1.0 | 400-W Hg lamp | 1.0 wt%  Ag | 0.1 M  NaHCO3 | 16.9 | 70.1 | 117 | 87.4 | 7 |
| SrO/Ta2O5 | 1.0 | 400-W Hg lamp | 3.0 wt%  Ag | 0.1 M  NaHCO3 | 3.80 | 5.10 | 6.80 | 64.2 | 8 |
| KCaSrTa5O15 | 0.5 | 400-W Hg lamp | 0.5 wt%  Ag | 0.1 M  NaHCO3 | 15.0 | 46.0 | 97.0 | 86.7 | 9 |
| ZnTa2O6 | 1.0 | 400-W Hg lamp | 1.0 wt%  Ag | 0.1 M  NaHCO3 | 25.1 | 18.6 | 19.3 | 43.4 | 10 |
| Sr2KTa5O15 | 1.0 | 400-W Hg lamp | 1.0 wt%  Ag | 0.1 M  NaHCO3 | 8.30 | 34.3 | 65.5 | 88.8 | 11 |
| K2YTa5O15 | 1.0 | 400-W Hg lamp | 1.0 wt%  Ag | 0.1 M  NaHCO3 | 16.2 | 43.2 | 91.9 | 85.0 | 12 |
| Sr1.6K0.37Na1.43Ta5O15 | 1.0 | 400-W Hg lamp | 1.0 wt%  Ag | 0.1 M  NaHCO3 | 16.0 | 53.7 | 94.6 | 85.5 | 13 |
| SrNb2O6 | 0.5 | 400-W Hg lamp | 0.5 wt%  Ag | 0.1 M  NaHCO3 | 1.10 | 24.8 | 51.2 | 97.9 | 14 |
| Mg-Al LDH/Ga2O3 | 1.0 | 400-W Hg lamp | 1.0 wt%  Ag | 0.1 M  NaHCO3 | 131 | 167 | 212 | 61.7 | 15 |
| Pr/Ga2O3 | 0.5 | 400-W Hg lamp | 1.0 wt%  Ag | 0.1 M  NaHCO3 | 64.7 | 150 | 249 | 79.4 | 16 |
| Yb-Zn/Ga2O3 | 0.5 | 400-W Hg lamp | 1.0 wt%  Ag | 0.1 M  NaHCO3 | 37.6 | 103 | 150 | 80.0 | 17 |
| Ga2O3 | 0.5 | 400-W Hg lamp | 1.0 mol%  (Ag-Cr) | 0.1 M  NaHCO3 | 92.9 | 281 | 480 | 83.8 | 18 |
| Ga2O3\_Ca | 0.5 | 400-W Hg lamp | 1.0 mol%  (Ag-Cr) | 0.1 M  NaHCO3 | 49.0 | 402 | 835 | 94.5 | This work |

a Estimated from the figure mentioned in the paper.

**Supplementary Table 2.** Comparison between the calculated Ca/Ga molar ratios and those measured by ICP-OES at different CaCl2 concentrations.

|  |  |  |
| --- | --- | --- |
| **CaCl2 concentration**  **(mol L−1)** | **Ca/Ga molar ratio (mol%)**  **(Calculated)** | **Ca/Ga molar ratio (mol%)**  **(ICP-OES)** |
| 0.0000 | 0.00 | 0.056 |
| 0.0005 | 0.31 | 0.32 |
| 0.0010 | 0.63 | 0.62 |
| 0.0020 | 1.3 | 1.1 |
| 0.0030 | 2.0 | 1.6 |
| 0.0050 | 3.3 | 2.1 |
| 0.0100 | 6.5 | 3.3 |

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**Supplementary Figure 1. Product formation rates and selectivities.** Formation rates of H2 (blue bars), O2 (green bars), and CO (red bars) and selectivity toward CO evolution (black diamonds) for the (a) Ag-Cr/Ga2O3, Ag-Cr/Ga2O3\_Ca\_*x* with a Ca/Ga molar ratio *x* of (b) 0.32 mol%, (c) 0.62 mol%, (d) 1.1 mol%, (e) 1.6 mol%, (f) 2.1 mol%, and (g) 3.3 mol%, and (h) Ag-Cr/CaGa4O7 during the photocatalytic conversion of CO2 by H2O. Amount of photocatalyst: 0.5 g; Volume of reaction solution (H2O): 1.0 L; Additive: 0.1 M NaHCO3; CO2 flow rate: 30 mL min−1; Light source: 400 W high-pressure Hg lamp.

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**Supplementary Figure 2**. **Product formation rates for 15 h.** Formation rates of CO (red circle) and H2 (blue triangle) for the photocatalytic conversion of CO2 by H2O over Ag@Cr/Ga2O3 (hollow mark) and Ag@Cr/Ga2O3\_Ca (solid mark).

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**Supplementary Figure 3.** **Various control experiments.** Formation rates of H2 (blue bars), O2 (green bars), and CO (red bars) for the Ag-Cr/Ga2O3\_Ca photocatalyst during photocatalytic conversion of CO2. The data markers ○ and × indicate the presence and absence of each component, respectively. Amount of photocatalyst: 0.5 g; Volume of reaction solution (H2O): 1.0 L; Additive: 0.1 M NaHCO3; CO2 flow rate: 30 mL min−1; Light source: 400 W high-pressure Hg lamp.

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**Supplementary Figure 4.** **BET specific surface areas.** BET specific surface areas for Ga2O3\_Ca\_*x* with a Ca/Ga molar ratio *x* of 0.056, 0.32, 0.62, 1.1, 2.1, and 3.3 mol%.

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**Supplementary Figure 5.** **FTIR spectra of CO2 adsorption**. CO2 adsorbed on: (a) Ga2O3, (b) Ga2O3\_Ca\_1.1, (c) CaO, (d) Ga2O3\_Ca\_3.3, and (e) CaGa4O7 after introducing the same amount of CO2 at various pressures in the 0.1–40.0 Torr range.

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**Supplementary Figure 6.** **Product formation rates and consumed electrons.** Formation rates of H2 (blue bars), O2 (green bars), and CO (red bars), as well as the consumed electrons (black diamonds) for (a) Ag-Cr/Ga2O3, Ag-Cr/Ga2O3\_Ca\_*x* with a Ca/Ga molar ratio *x* of (b) 0.32 mol%, (c) 0.62 mol%, (d) 1.1 mol%, (e) 1.6 mol%, (f) 2.1 mol%, and (g) 3.3 mol%, and (h) Ag-Cr/CaGa4O7 during photocatalytic conversion of CO2 by H2O. Amount of photocatalyst: 0.5 g; Volume of reaction solution (H2O): 1.0 L; Additive: 0.1 M NaHCO3; CO2 flow rate: 30 mL min−1; Light source: 400 W high-pressure Hg lamp.

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**Supplementary Figure 7.** **Mott-Schottky plots of photocatalysts.** Mott-Schottky plot for (a) Ga2O3/FTO, (b) Ga2O3\_Ca\_0.62/FTO, and (c) CaGa4O7/FTO based on the results of the impedance measurements at a frequency of (ⅰ) 39.8, (ⅱ) 31.6, and (ⅲ) 25.1 kHz. Electrolyte solution: Na2SO4 *aq*. (0.1 M, pH ca.7.0, Ag/AgCl), atmosphere: N2.

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**Supplementary Figure 8.** **Determination of band gap.** (a) UV-visible spectra and (b) Davis-Mott plot presenting (αhv)2 versus photon energy for the determination of band gap of Ga2O3 (black line), Ga2O3\_Ca\_0.62 (red line), and CaGa4O7 (blue line).

**文字と写真のスクリーンショット

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**Supplementary Figure 9.** **Band positions of photocatalysts.** Conduction band and valence band positions of Ga2O3, Ga2O3\_Ca\_0.62, and CaGa4O7.

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**Supplementary Figure 10. Isotopic lead experiments.** Gas chromatogram and mass spectra (m/z = 28 and 29) in the photocatalytic conversion of 13CO2 by H2O over the CaGa4O7/Ga2O3 photocatalyst physically mixed with 30 mol% of CaO with 1.0 mol% Ag-Cr as the cocatalyst.

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