Electronic Supplementary Information (ESI)

Drastic Improvement in the Photocatalytic Activity of Ga$_2$O$_3$ Modified with Mg–Al Layered Double Hydroxide for the Conversion of CO$_2$ in Water

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Figure S1 UV/Vis spectra of (A) 0.25Ag/95-MgAl/Ga₂O₃, (B) 95-MgAl/Ga₂O₃, (C) Mg–Al LDH, and (D) Ga₂O₃. UV/Vis diffuse reflectance spectra of the photocatalysts were measured using a UV-VIS Spectrophotometer (V-650, JASCO) equipped with an integrated sphere. BaSO₄ plate was used as a standard baseline for these spectra.
Figure S2 TEM images of (a) 1.0Ag/Ga₂O₃, (b) 1.0Ag/30-MgAl/Ga₂O₃, (c) 1.0Ag/95-MgAl/Ga₂O₃, (d) 0.25Ag/95-MgAl/Ga₂O₃, (e) 1.0Ag/95-MgAl/Ga₂O₃, and (f) 3.0Ag/95-MgAl/Ga₂O₃, captured on JEM-2100F TEM system (Japan Electron Optics Laboratory).
Figure S3 Ag 3d X-ray photoelectron spectra of (a) Ag powder, (b) Ag₂O, (c) 0.25Ag/95-MgAl₂Ga₂O₃, and (d) 0.25Ag/95-MgAl₂Ga₂O₃ after photoirradiation for 5 h. X-ray photoelectron spectra of composite photocatalysts were measured by ESCA-3400 (Shimadzu) using Mg Kα characteristic X-ray radiation. Peak positions were corrected by using C 1s peaks.
Figure S4 Surface atomic ratio of Ag cocatalyst loaded $x$-MgAl/Ga$_2$O$_3$ composite photocatalysts ($x = 0, 30, 50, 70, 95$) and bare Mg–Al LDH. X-ray photoelectron spectra of composite photocatalysts were measured by ESCA-3400 (Shimadzu) using Mg $K_\alpha$ characteristic X-ray radiation. Surface atomic ratios of elements were calculated using the following equations.

$$ A_{\text{total}} = A_{\text{Ag}} + A_{\text{Ga}} + A_{\text{Mg}} + A_{\text{Al}} $$

$$ \text{Ag} \ (%) = 100 \times \frac{A_{\text{Ag}}}{A_{\text{total}}} $$

$$ \text{Ga} \ (%) = 100 \times \frac{A_{\text{Ga}}}{A_{\text{total}}} $$

$$ \text{Mg} + \text{Al} \ (%) = 100 \times \frac{(A_{\text{Mg}} + A_{\text{Al}})}{A_{\text{total}}} $$

where $A_{\text{Ag}}, A_{\text{Ga}}, A_{\text{Mg}},$ and $A_{\text{Al}}$ are peak areas in the spectra attributed to Ag 3d, Ga 2p, Mg 2p, and Al 2p, respectively.
Figure S5 Anodic photocurrent value of Ag cocatalyst loaded $x$-MgAl/Ga$_2$O$_3$ composite photocatalysts ($x = \rightarrow$: 0, \rightarrow: 30, \rightarrow: 50, \rightarrow: 70, \rightarrow: 95) with on/off UV light irradiation in the presence of methanol in the electrolyte solution. The composite photocatalysts were coated on a fluorine doped tin oxide (FTO) conductive glass by the electrophoresis deposition. The powder sample of the composite photocatalyst was dispersed thoroughly in an acetone solution containing iodine (I$_2$), and then direct current (DC) was applied to the FTO glasses, which comprised two-electrode electrochemical cell, at 10.0 V stable bias. Photocurrent value was measured by using three-electrode electrochemical cell under the photoirradiation by 200 W Hg-Xe lamp through quartz glass window. The obtained anodic photocurrent values were normalized by the weight of Ga$_2$O$_3$ contained in the composite photocatalysts.
Table S1

The result of photocatalytic conversion of CO$_2$ in water for 0.25Ag/95-MgAl/Ga$_2$O$_3$ composite photocatalyst and a series of reference photocatalysts. The content of Ga$_2$O$_3$ in photocatalyst powder was fixed at 0.19 g. Reaction solution: 1.0 L of aqueous NaHCO$_3$ solution (0.1 M), CO$_2$ supply: 30 mL min$^{-1}$, light source: 400 W high-pressure Hg lamp (through quartz glass jacket), photoirradiation time: 1 h.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Type</th>
<th>Weight / g</th>
<th>Formation rate / µmol h$^{-1}$</th>
<th>Selectivity to CO (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Total</td>
<td>Ga$_2$O$_3$</td>
<td>H$_2$</td>
</tr>
<tr>
<td>95-MgAl/Ga$_2$O$_3$</td>
<td>composite</td>
<td>1.0</td>
<td>0.19</td>
<td>534.9</td>
</tr>
<tr>
<td>0.25Ag/95-MgAl/Ga$_2$O$_3$</td>
<td>composite</td>
<td>1.0</td>
<td>0.19</td>
<td>131.2</td>
</tr>
<tr>
<td>95-MgAl/0.25Ag/Ga$_2$O$_3$</td>
<td>composite</td>
<td>1.6</td>
<td>0.19</td>
<td>148.0</td>
</tr>
<tr>
<td>95-MgAl + 0.25Ag/Ga$_2$O$_3$</td>
<td>mixture</td>
<td>1.0</td>
<td>0.19</td>
<td>348.2</td>
</tr>
<tr>
<td>0.25Ag/Ga$_2$O$_3$</td>
<td>bare</td>
<td>0.19</td>
<td>0.19</td>
<td>130.7</td>
</tr>
<tr>
<td>1.0Ag/Mg$_2$Al LDH</td>
<td>bare</td>
<td>0.50</td>
<td>0.00</td>
<td>trace</td>
</tr>
</tbody>
</table>
Figure S6 Schematic illustrations of 0.25Ag/Ga$_2$O$_3$ (bare photocatalyst), 95-MgAl/0.25Ag/Ga$_2$O$_3$ (reference composite photocatalyst), 95-MgAl + 0.25Ag/Ga$_2$O$_3$ (mixture photocatalyst), and 0.25Ag/95-MgAl/Ga$_2$O$_3$ (composite photocatalyst).
Figure S7 The amounts of products evolved (left axis) and the selectivity toward CO evolution (right axis) in the repeating test for the photocatalytic conversion of CO\(_2\) in water using 0.25Ag/95-MgAl/Ga\(_2\)O\(_3\) photocatalyst. Red circle: CO, green square: O\(_2\), blue triangle: H\(_2\), black diamond: selectivity toward CO evolution. Photocatalyst weight: 1.0 g, reaction solution: 1.0 L of an aqueous NaHCO\(_3\) solution (0.1 M), CO\(_2\) supply: 30 mL min\(^{-1}\), light source: 400 W high-pressure Hg lamp (through a quartz glass jacket). The reaction solution was thoroughly degassed by a flow of high-purity CO\(_2\) gas after 1st and 2nd run.
Figure S8 TEM images of (a) before and (b) after reaction for 0.25Ag/95-MgAl/Ga₂O₃, and (c) before and (d) after reaction for 1.0Ag/95-MgAl/Ga₂O₃, captured on JEM-2100F TEM system (Japan Electron Optics Laboratory).