Supporting Information

Selective electro- or photo-reduction of carbon dioxide to formic acid using Cu-Zn alloy catalyst

Ge Yin†, Hideki Abe§*, Rajesh Kodiyath§, Shigenori Ueda†, Nagarajan Srinivasan†, Akira Yamaguchi†, Masahiro Miyauchi**

† Department of Materials Science and Engineering, School of Materials and Chemical Technology, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8552, Japan.
§ Advanced Electronic Materials Center, National Institute of Materials Science, 1-1 Namiki, Tsukuba 305-004, Japan
‡ Synchrotron X-ray Station at SPring-8, National Institute for Materials Science, 1-1-1 Kouto, Sayo, Hyogo, 679-5148, Japan

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*To whom correspondence should be addressed, Email: mmiyauchi@ceram.titech.ac.jp; ABE.Hideki@nims.go.jp
Figure S1. The Photoelectrochemical (PEC) cell construction.

Figure S2. The light spectrum of the UV light used in the PEC cell and photocatalytic evaluation.
Figure S3. The construction of the gas-flow reactor used in the *in situ* FTIR analysis.

Figure S4. The produced amounts of Cu$_5$Zn$_8$ electrode from the PEC cell at rest potential, under CO$_2$ purging (■), under Ar purging (▲). a) HCOOH, b) CO, c) CH$_4$, d) H$_2$. 
Figure S5. The produced a) CO, b) CH₄, c) H₂ amounts of Cu₅Zn₈ electrode from the PEC cell at rest potential in CO₂-purged 0.1 M KHCO₃. PEC cells equipped with a pure Cu cathode and a pure Zn cathode as the electrolyte were used as controls.

Figure S6. Results of an isotope tracing experiment for the Cu-Zn catalyst decorated SrTiO₃, showing that ^{13}CO (m/z=29) and ^{18}O₂ (m/z=36) were detected among the reactions products under UV irradiation when ^{13}CO₂ was used as gas source and H₂^{18}O was used as water source.
Figure S7. The XPS Cu 2p and Zn 2p spectra of the Cu-Zn catalyst decorated SrTiO$_3$ after the CO$_2$ reduction reaction. Measurement condition: 10 cycles, 3 repetitions, one step=-0.15eV, 40ms.

Figure S8. a) The XRD pattern of Cu-Zn nanoparticles loaded SrTiO$_3$ (5%wt). The reflection peak at 43.23° correspond to the main peak of Cu$_5$Zn$_8$, peak at 36.15° correspond to pure Zn. Other peaks correspond to SrTiO$_3$. b) TEM graph of prepared Cu-Zn nanoparticles loaded SrTiO$_3$ powder. c) TEM graph of prepared Cu-Zn nanoparticles loaded SrTiO$_3$ powder, d) the EDX element analysis was operated inside the red circle of c).
**Figure S9.** The FT-IR spectra of a) Cu-Zn nanoparticles loaded SrTiO$_3$ powders and b) Cu nanoparticles loaded SrTiO$_3$ powders, measured in wet CO$_2$ atmosphere under UV irradiation. Spectra measured in wet CO$_2$ without UV irradiation and those in wet Ar under UV irradiation were used as control group.

When the Cu-Zn nanoparticles loaded SrTiO$_3$ powders was put in humid CO$_2$ and irradiated by UV light, peak appeared at 1280cm$^{-1}$, but didn’t appear in control groups and the spectra of Cu SrTiO$_3$. According to the FT-IR database and previous studies, this peak assigned to bidentate surface carbonate. This result was consistent with our proposal of the CO$_2$ to HCOOH reaction route, as shown in the manuscript Fig.7. As for the Cu nanoparticles loaded SrTiO$_3$, the presence of monodentate surface carbonate, the initiate of the CO and CH$_4$ routes, was proved by the peak appeared at 1442cm$^{-1}$. 
Table S1. The XRF results (mass%) of the composition analysis of Cu-Zn alloy electrodes prepared under different heating temperature.

<table>
<thead>
<tr>
<th>Heating temperature (˚C)</th>
<th>Cu</th>
<th>Zn</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>97.32</td>
<td>2.68</td>
<td>-</td>
</tr>
<tr>
<td>450</td>
<td>76.73</td>
<td>23.27</td>
<td>-</td>
</tr>
<tr>
<td>500</td>
<td>47.81</td>
<td>52.19</td>
<td>-</td>
</tr>
<tr>
<td>520*</td>
<td>0.86</td>
<td>4.21</td>
<td>94.9-</td>
</tr>
</tbody>
</table>

*The sample under 520˚C was measured at different time with others. In this case Ti composition was also measured. The Zn concentration used in Fig 2d was calculated as 4.21/(4.21+0.86)*100%=83.04%.

Table S2. The XRF and ICP results of the composition analysis of Cu-Zn alloy nanoparticles loaded SrTiO₃.

<table>
<thead>
<tr>
<th></th>
<th>Cu</th>
<th>Zn</th>
<th>Ti</th>
<th>Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-ray Fluorescence (mass%)</td>
<td>0.54</td>
<td>1.54</td>
<td>22.9</td>
<td>75.1</td>
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<tr>
<td>Inductively Coupled Plasma (mg in 1.562mg sample)</td>
<td>0.0070</td>
<td>0.0174</td>
<td>0.363</td>
<td>0.670</td>
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References