Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

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

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Copper, zinc, Cu-Zn alloy, CO_2 reduction, electrocatalytic, photoelectrochemical, photocatalytic.

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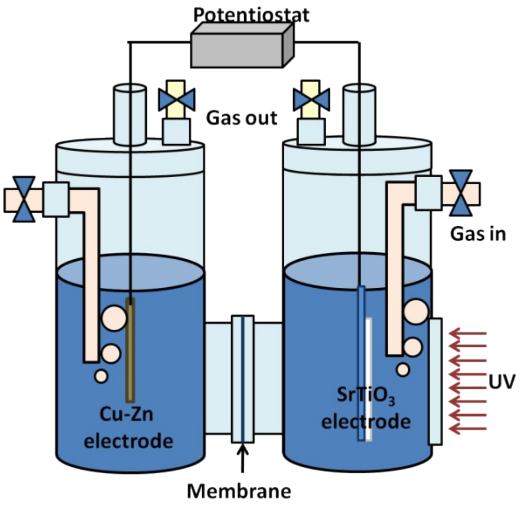

Figure S1. The Photoelectrochemical (PEC) cell construction.

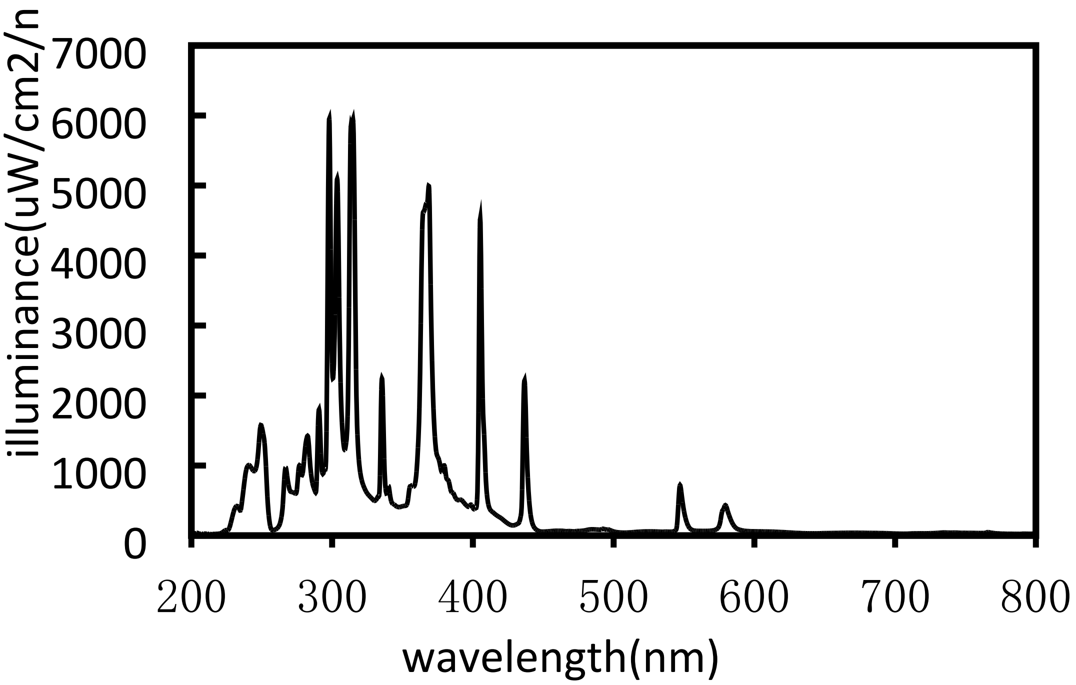

Figure S2. The light spectrum of the UV light used in the PEC cell and photocatalytic evaluation.

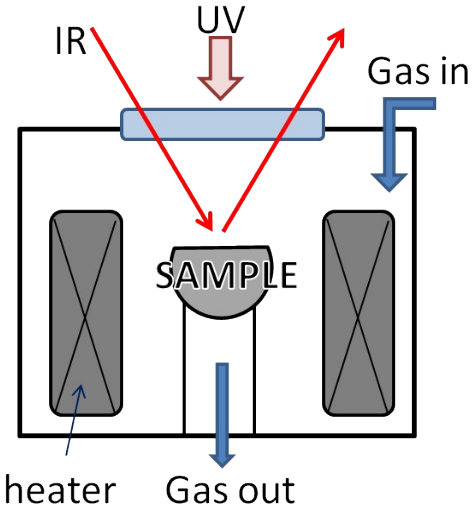

Figure S3. The construction of the gas-flow reactor used in the *in situ* FTIR analysis.

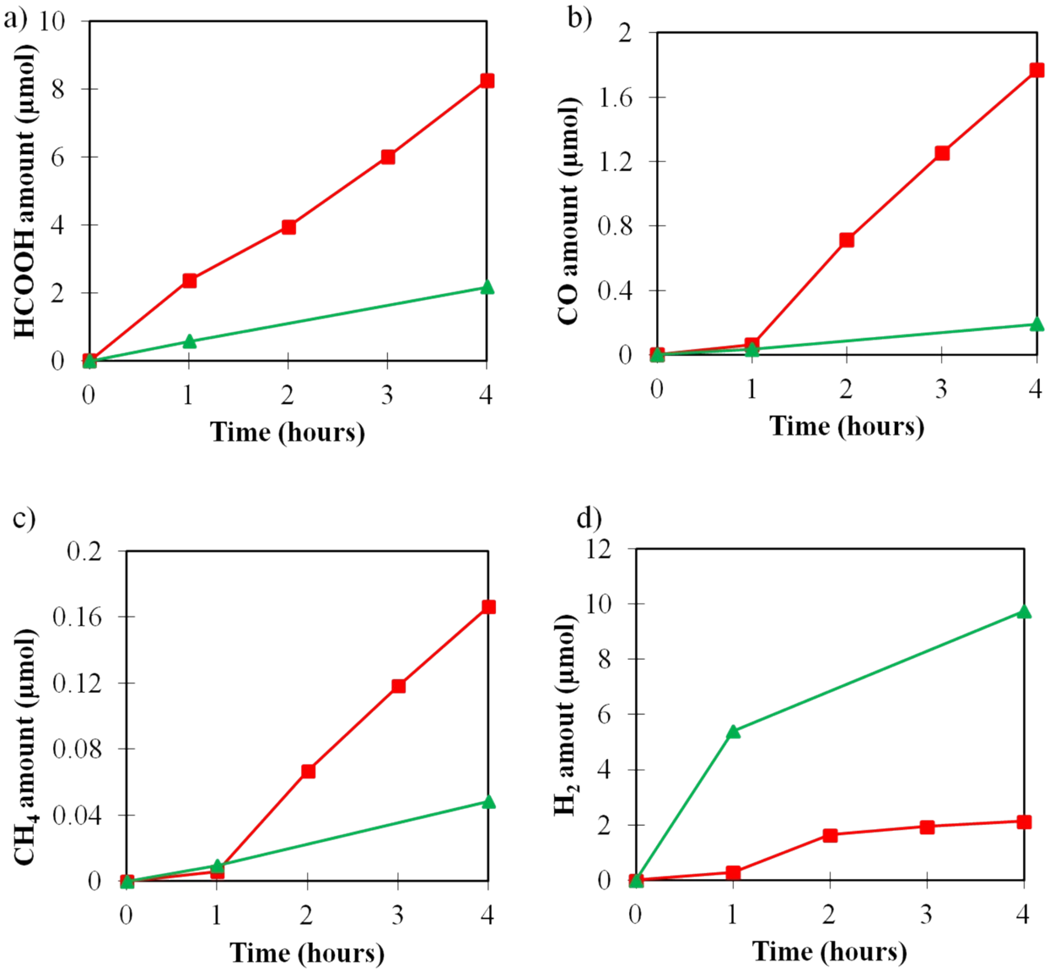

Figure S4. The produced amounts of Cu_5Zn_8 electrode from the PEC cell at rest potential, under CO_2 purging (🟥), under Ar purging (▲). a) HCOOH, b) CO, c) CH_4, d) H_2.

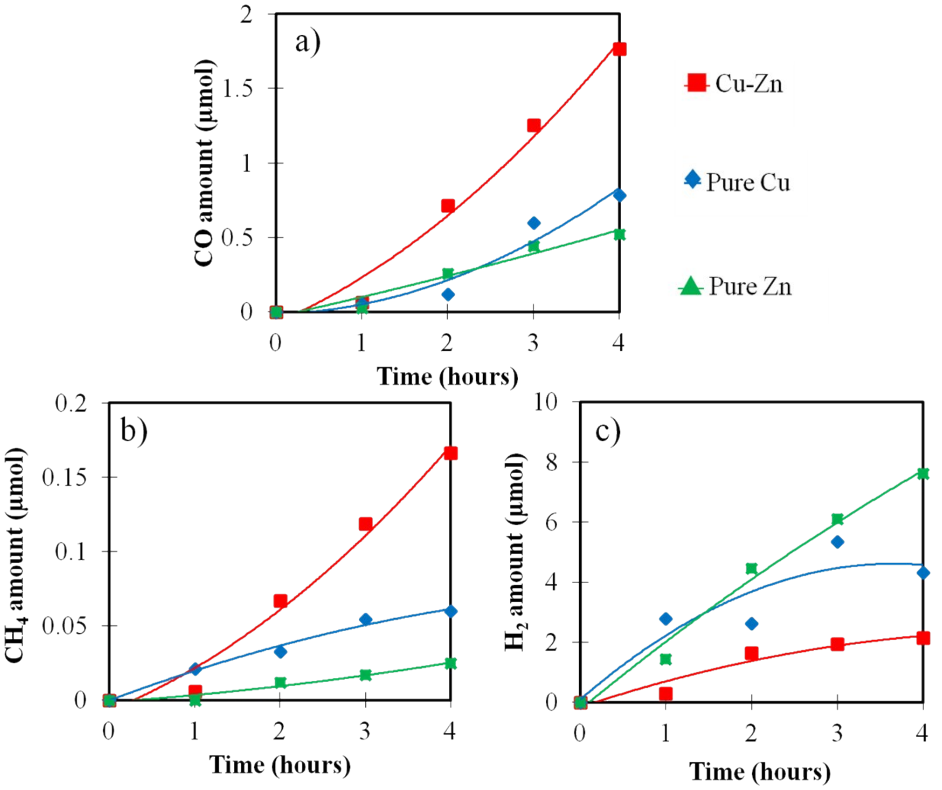

Figure S5. The produced a) CO, b) CH_4, c) H_2 amounts of Cu_5Zn_8 electrode from the PEC cell at rest potential in CO_2-purged 0.1 M $KHCO_3$. PEC cells equipped with a pure Cu cathode and a pure Zn cathode as the electrolyte were used as controls.

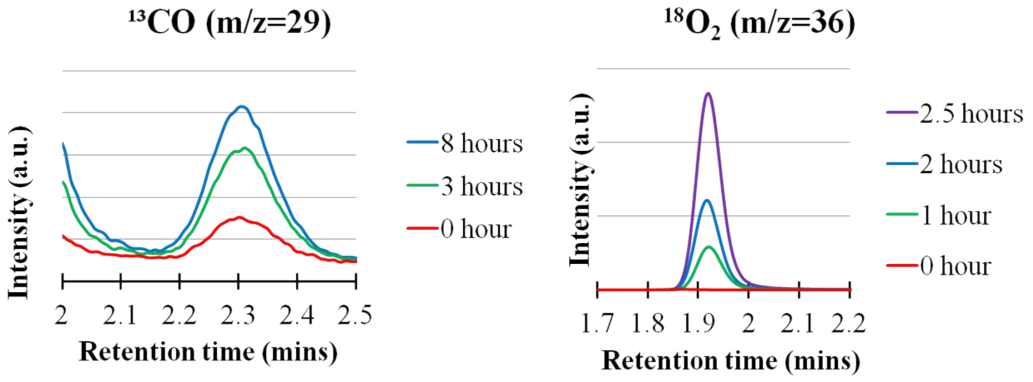

Figure S6. Results of an isotope tracing experiment for the Cu-Zn catalyst decorated $SrTiO_3$, showing that ^{13}CO (m/z=29) and $^{18}O_2$ (m/z=36) were detected among the reactions products under UV irradiation when $^{13}CO_2$ was used as gas source and $H_2{}^{18}O$ was used as water source.

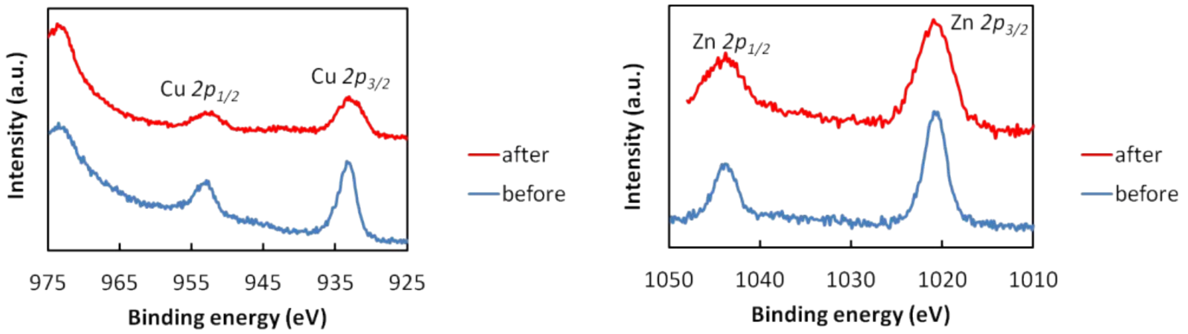

Figure S7. The XPS Cu *2p* and Zn *2p* spectra of the Cu-Zn catalyst decorated $SrTiO_3$ after the CO_2 reduction reaction. Measurement condition: 10 cycles, 3 repetitions, one step=-0.15eV, 40ms.

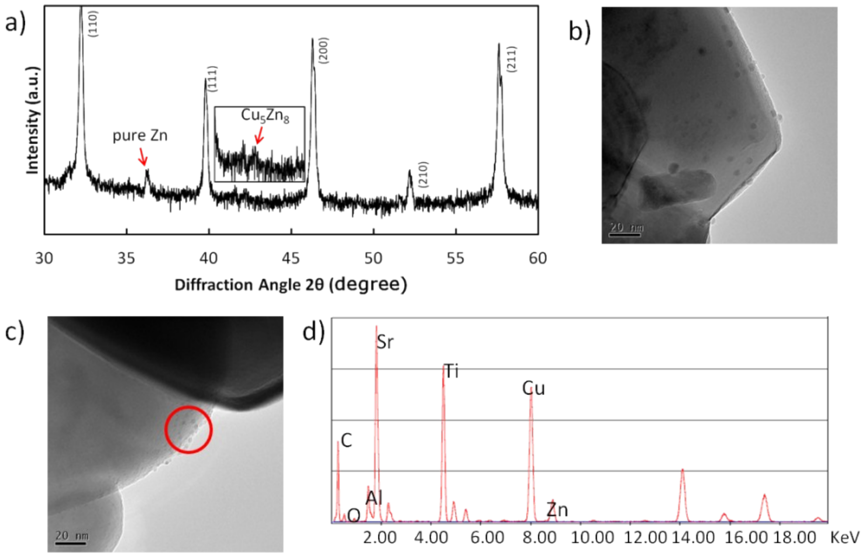

Figure S8. a) The XRD pattern of Cu-Zn nanoparticles loaded $SrTiO_3$ (5%wt). The reflection peak at 43.23˚ correspond to the main peak of Cu_5Zn_8, peak at 36.15˚ correspond to pure Zn. Other peaks correspond to $SrTiO_3$.b) TEM graph of prepared Cu-Zn nanoparticles loaded $SrTiO_3$ powder. c) TEM graph of prepared Cu-Zn nanoparticles loaded $SrTiO_3$ powder, d) the EDX element analysis was operated inside the red circle of c).

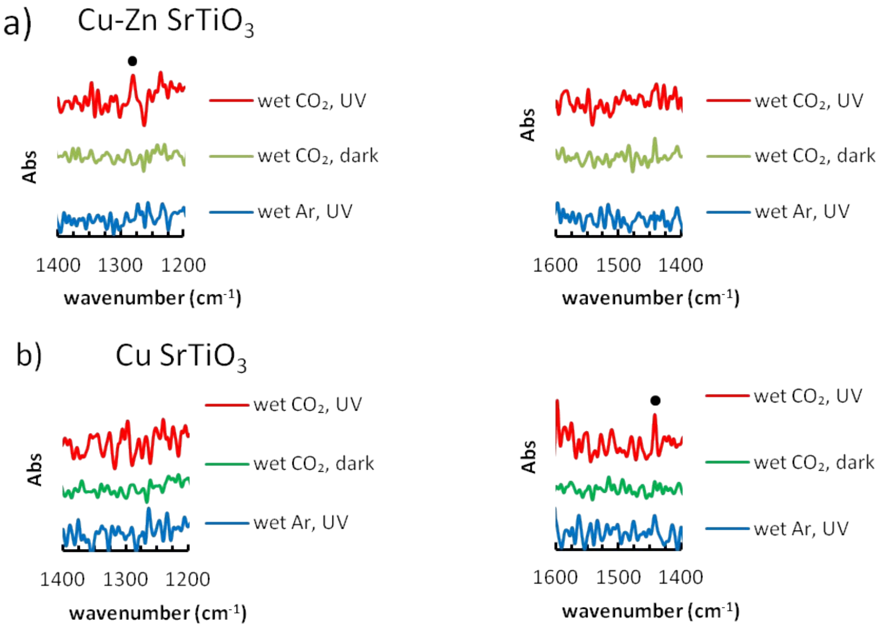

Figure S9. The FT-IR spectra of a) Cu-Zn nanoparticles loaded $SrTiO_3$ powders and b) Cu nanoparticles loaded $SrTiO_3$ powders, measured in wet CO_2 atmosphere under UV irrdiation. Spectra measured in wet CO_2 without UV irradiation and those in wet Ar under UV irradiation were used as control group.

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.

Heating temperature (˚C)	Cu	Zn	Ti
400	97.32	2.68	-
450	76.73	23.27	-
500	47.81	52.19	-
520*	0.86	4.21	94.9-

*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 $SrTiO_3$.

Cu	Zn	Ti	Sr
X-ray Fluorescence (mass%)			
0.54	1.54	22.9	75.1
Inductively Coupled Plasma (mg in 1.562mg sample)			
0.0070	0.0174	0.363	0.670

References

1. Schild, C.; Wokaun, A.; Baiker, A., *Journal of Molecular Catalysis* **1990,** *63* (2), 243-254.
2. Du, H.; Williams, C. T.; Ebner, A. D.; Ritter, J. A., *Chemistry of Materials* **2010,** *22* (11), 3519-3526.