

Supporting information

Effect of Zn in Ag-Loaded Zn-Modified ZnTa₂O₆ for Photocatalytic Conversion of CO₂ by H₂O

Shuying Wang[†], Kentaro Teramura^{†,‡*}, Hiroyuki Asakura^{†,‡}, Saburo Hosokawa^{†,‡},
Tsunehiro Tanaka^{†,‡*}

[†]Department of Molecular Engineering, Graduate School of Engineering, Kyoto University,
Kyotodaigaku Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

[‡]Element Strategy Initiative for Catalysts & Batteries (ESICB), Kyoto University, 1-30
Goryo-Ohara, Nishikyo-ku, Kyoto 615-8245, Japan

E-mail address: teramura@moleng.kyoto-u.ac.jp; tanakat@moleng.kyoto-u.ac.jp

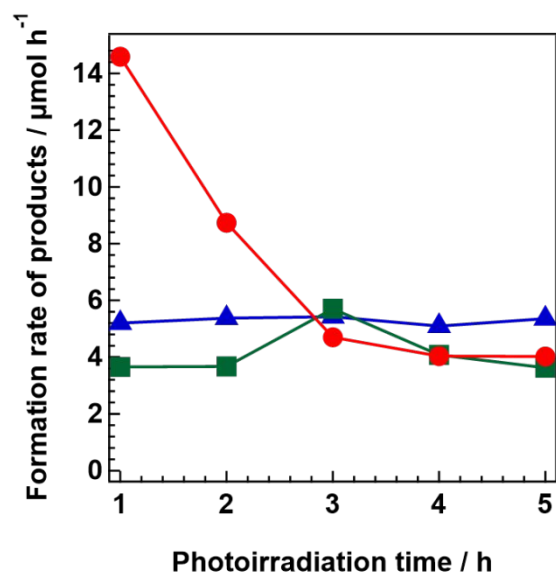


Figure S1. Time-dependent evolution of H_2 (blue), O_2 (green), and CO (red) 3.0Ag/
 $\text{Zn}_3\text{Ta}_2\text{O}_8$

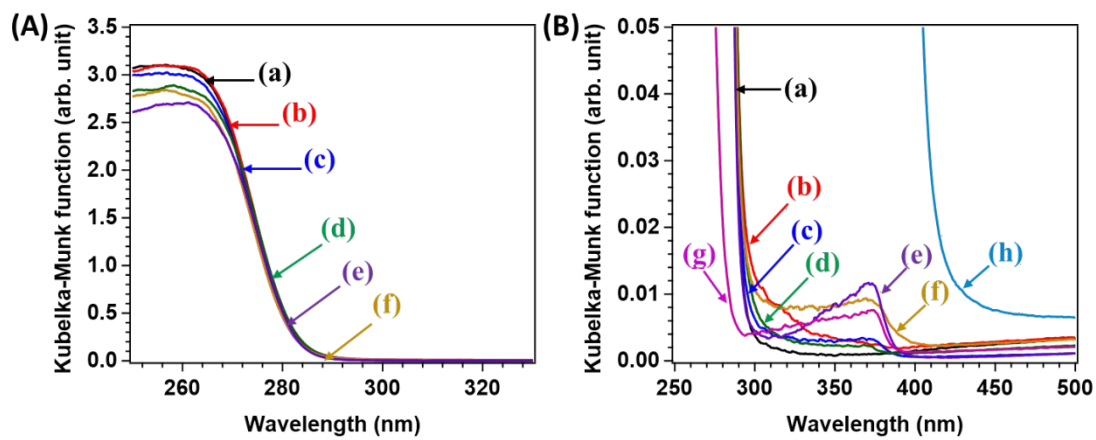


Figure S2 UV-vis spectra of (a) ZnTa₂O₆, (b) 2.5Zn/ZnTa₂O₆, (c) 10Zn/ZnTa₂O₆, (d) 15Zn/ZnTa₂O₆, (e) 20Zn/ZnTa₂O₆, (f) 40Zn/ZnTa₂O₆, (g) Zn₃Ta₂O₈, (h) ZnO

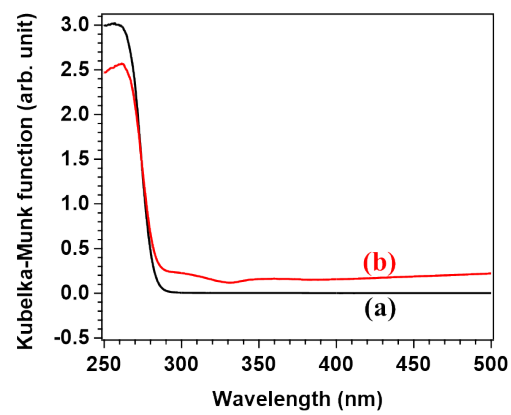


Figure S3 UV-vis spectra of (a) 10Zn/ZnTa₂O₆; (b) Ag/10Zn/ZnTa₂O₆

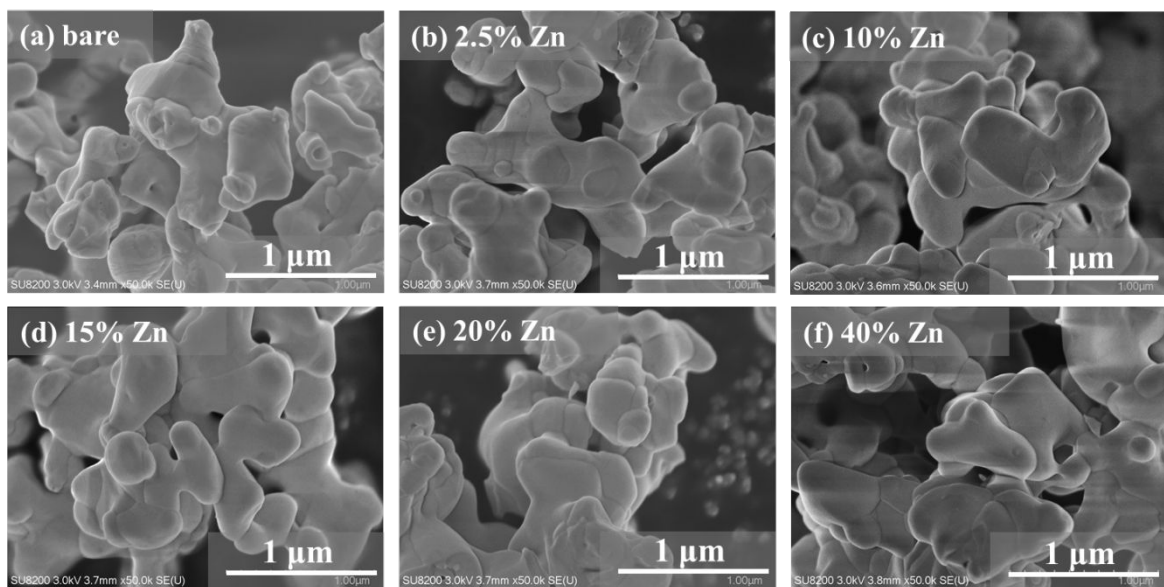


Figure S4 SEM images of the (a) ZnTa_2O_6 , (b) $2.5\text{Zn}/\text{ZnTa}_2\text{O}_6$, (c) $10\text{Zn}/\text{ZnTa}_2\text{O}_6$, (d) $15\text{Zn}/\text{ZnTa}_2\text{O}_6$, (e) $20\text{Zn}/\text{ZnTa}_2\text{O}_6$, (f) $40\text{Zn}/\text{ZnTa}_2\text{O}_6$,

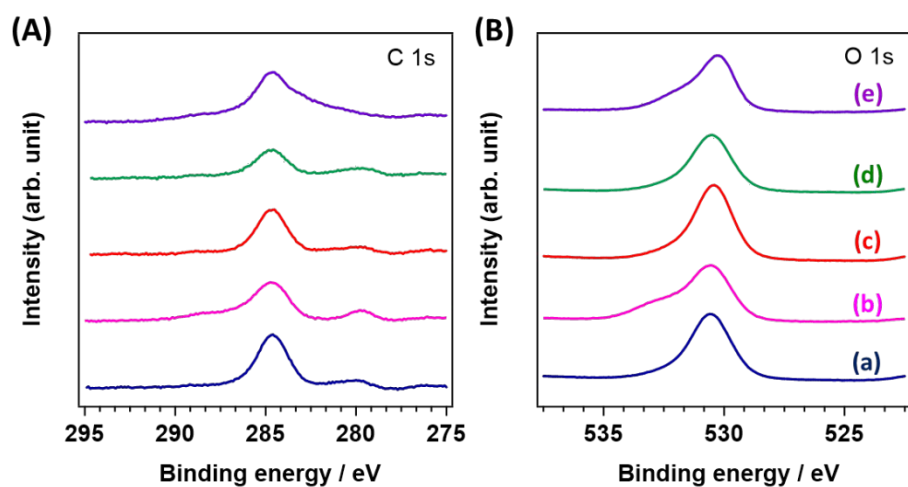


Figure S5. XPS spectra of (A) C 1s and (B) O 1s for (a) ZnTa_2O_6 , (b) $10\text{Zn}/\text{ZnTa}_2\text{O}_6$ without calcination; (c) $10\text{Zn}/\text{ZnTa}_2\text{O}_6$, (d) $\text{Zn}_3\text{Ta}_2\text{O}_8$, and (e) ZnO

Table S1. The ratio of Zn to Ta detected by EDS and XPS

	Zn/Ta in theory	Zn/Ta by EDS	Zn/Ta by XPS	BET / m ² g ⁻¹
ZnTa ₂ O ₆	0.50	0.50	0.63	2.5
10Zn/ZnTa ₂ O ₆	0.55	0.57	1.24	2.2
3.0Ag/10Zn/ZnTa ₂ O ₆	0.55	0.57	1.01	/
Zn ₃ Ta ₂ O ₈	1.50	1.54	2.61	/

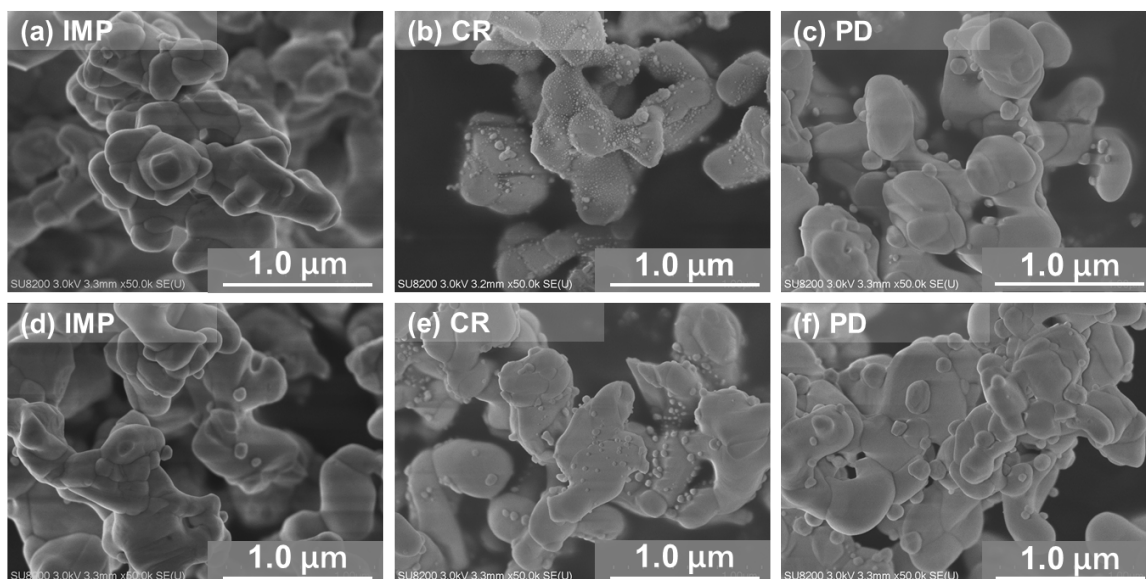


Figure S6. SEM images of (a), (d) 1.5Ag/10Zn/ZnTa₂O₆ (IMP method); (b), (e) 1.5Ag/10Zn/ZnTa₂O₆ (CR method); and (c), (f) 1.5Ag/10Zn/ZnTa₂O₆ (PD method). (a–c) before reaction, and (d–f) after reaction.

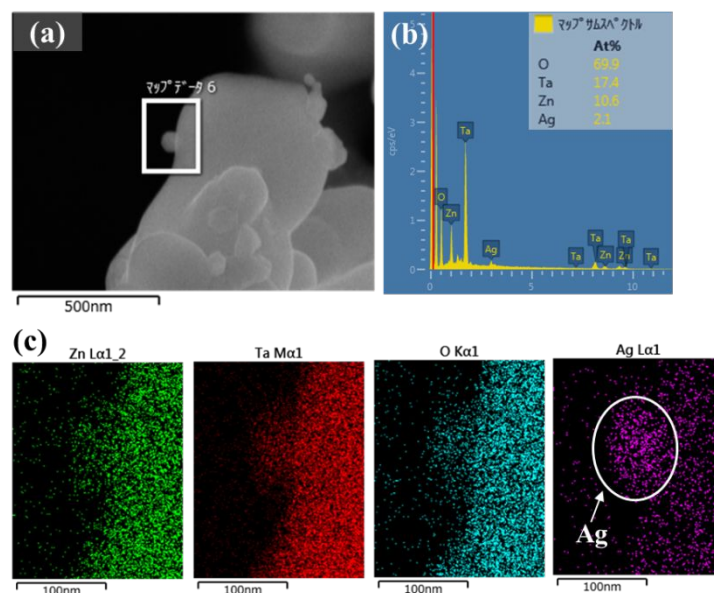


Figure S7. (a) 3.0Ag/10Zn/ZnTa₂O₆: Zn prepared by IMP method, after reaction; (b) EDS mapping of the Ag-loaded ZnTa₂O₆: Zn after photocatalytic reactions; (c) EDS mapping of the Zn, Ta, O, and Ag element

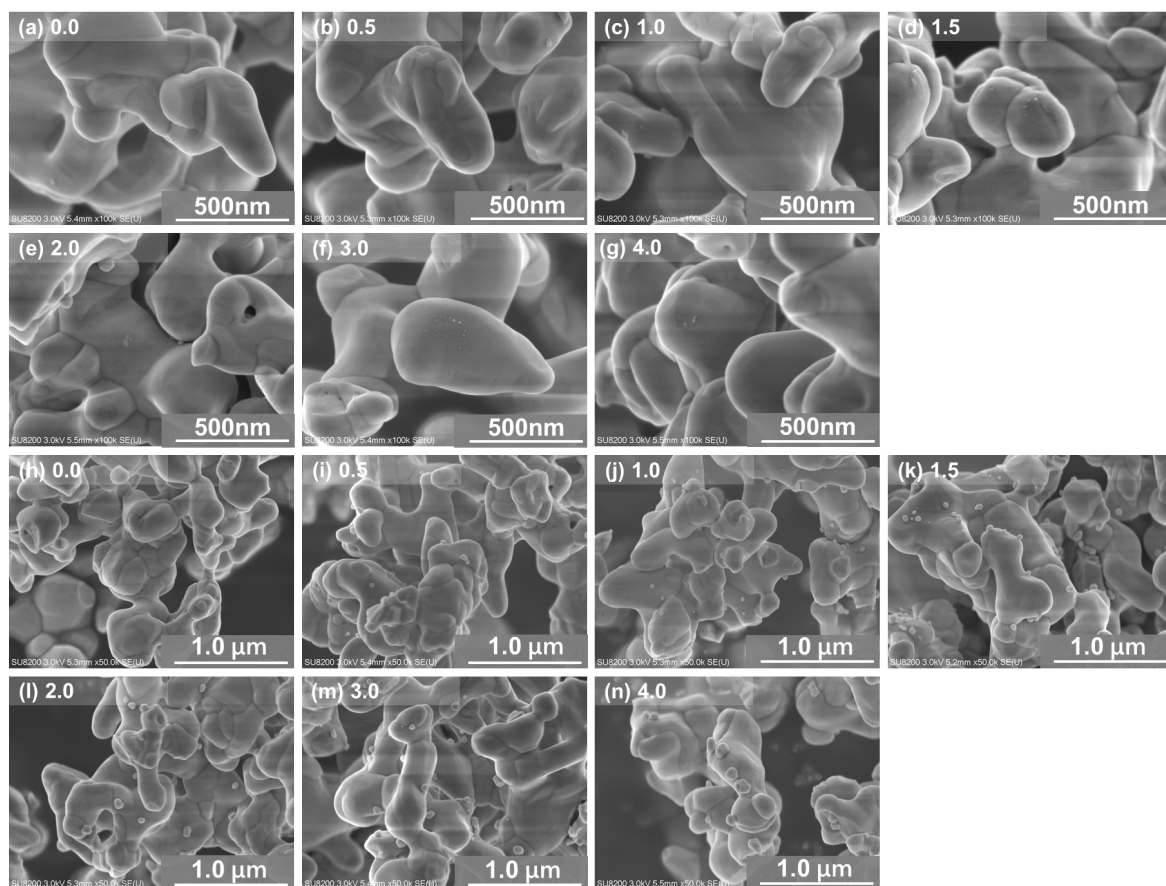


Figure S8. SEM image of the 10Zn/ZnTa₂O₆ loaded with various amount of Ag cocatalyst (a-g) before reaction; (h-n) After 5-h photocatalytic reaction. (a) and (h) 0.0Ag; (b) and (i) 0.5Ag; (c) and (j) 1.0Ag; (d) and (k) 1.5Ag; (e) and (l) 2.0Ag; (f) and (m) 3.0Ag; (g) and (n) 4.0Ag.

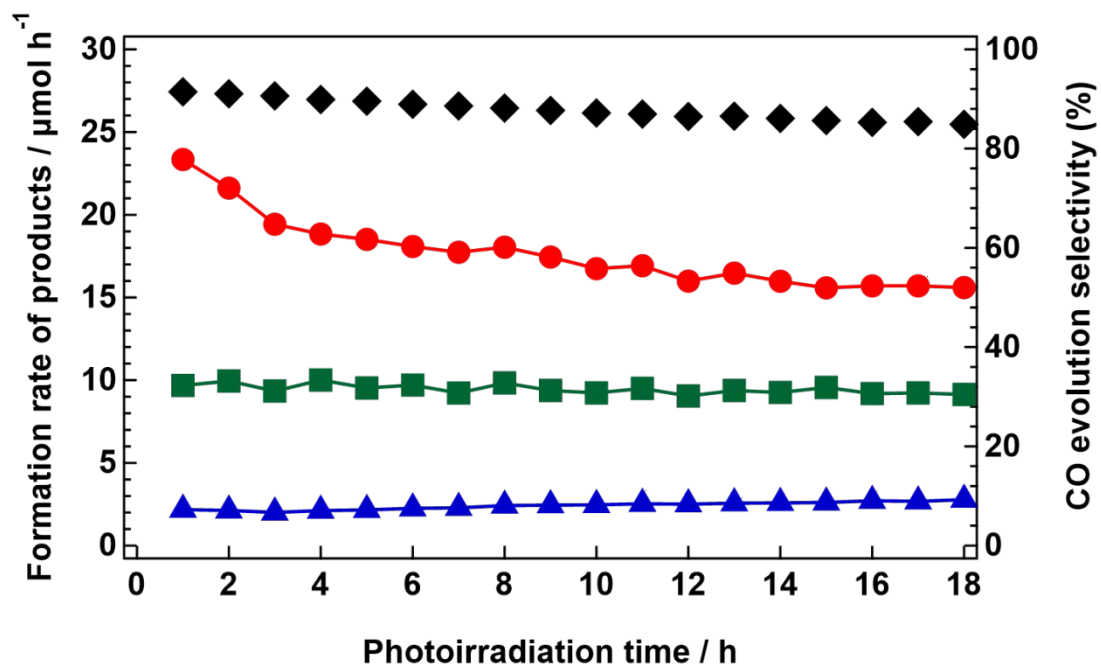


Figure S9. Time-dependent evolution of H₂ (blue), O₂ (green), and CO (red) over 3.0Ag/10Zn/ZnTa₂O₆

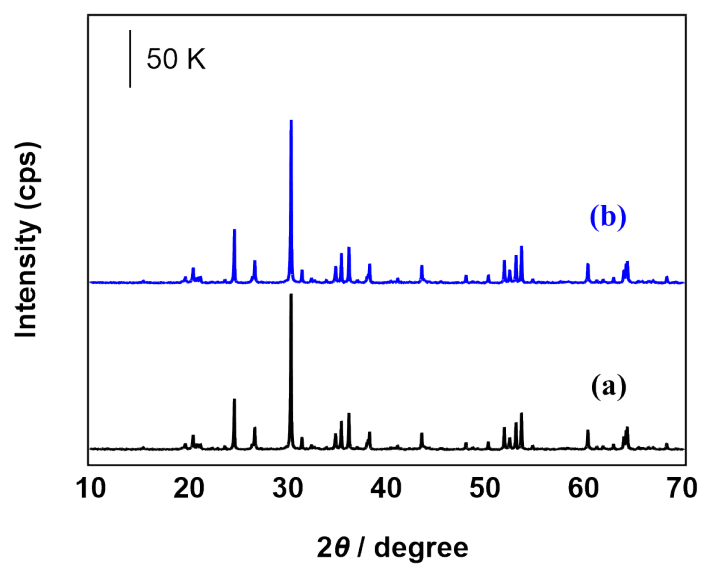


Figure S10. XRD patterns of $3.0\text{Ag}/10\text{Zn}/\text{ZnTa}_2\text{O}_6$ (a) before and (b) after 15 h photocatalytic reaction.

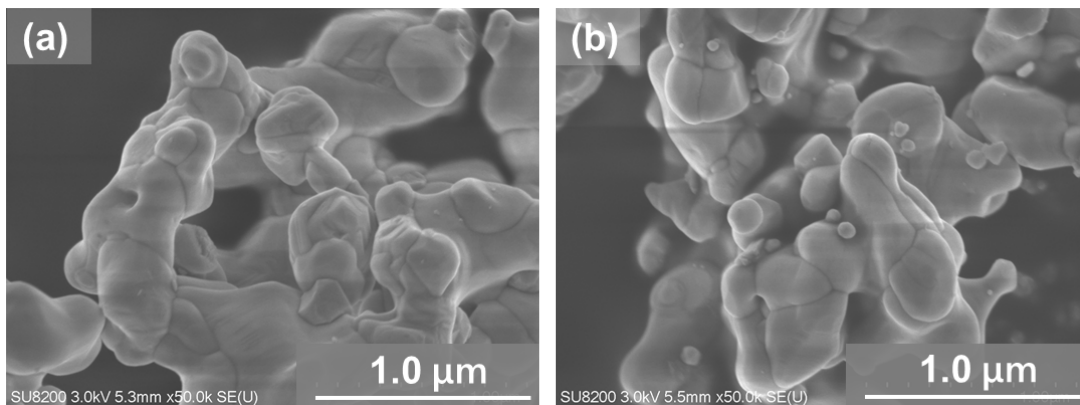


Figure S11. SEM images of 3.0Ag/10Zn/ZnTa₂O₆ (a) before and (b) after 15 h photocatalytic reaction.

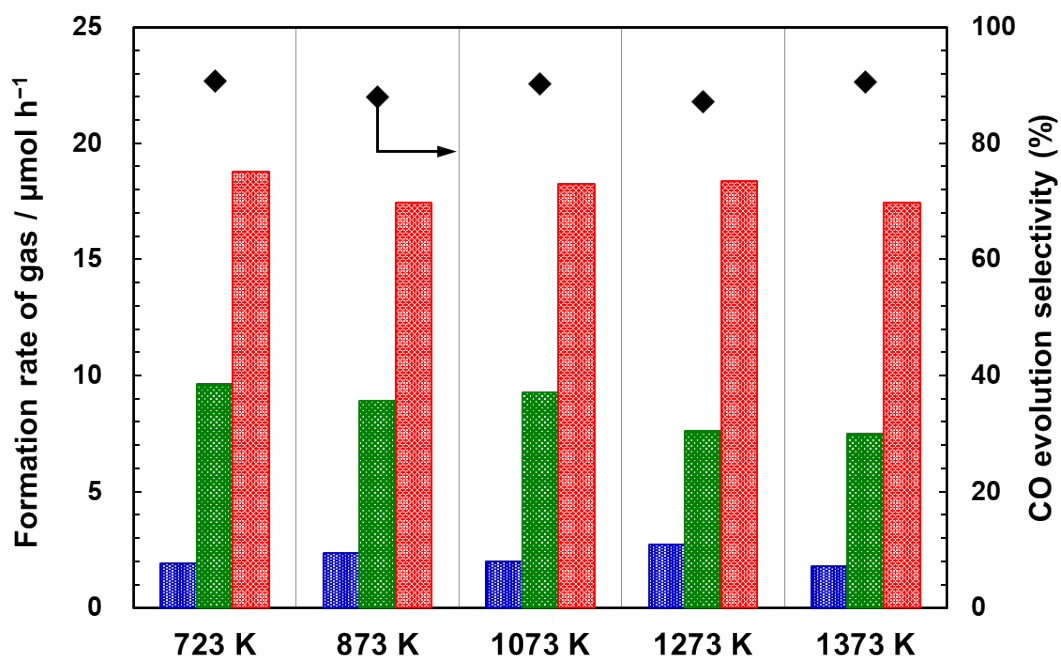
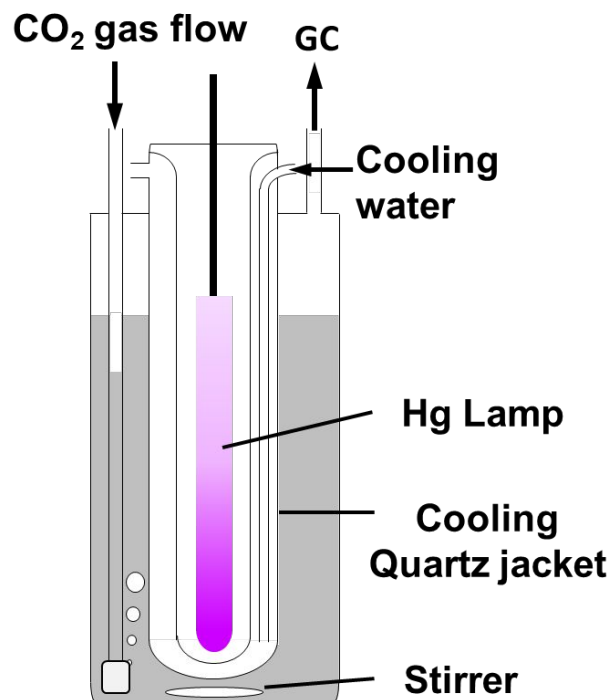


Figure S12 the formation rate of H₂ (blue), O₂ (green), and CO (red) over the Ag/Zn/ZnTa₂O₆ fabricated at various kinds calcination temperature.

Scheme S1. The scheme of the inner irradiation reactor



The formation rates of the products (CO, H₂ and O₂) were calculated by the follow equation:

$$\text{Formation rate of products / mol h}^{-1} = S \cdot c^* / (1 \text{ mL}) \cdot (30 \text{ mL/min}) \cdot 60 \text{ min}$$

Where S represents the peak area of gas products detected by the TCD-GC, and FID-GC, c represents a factor of the relationship between the amount of the gas products and the peak area of gas products such as CO, H₂, and O₂. The factor c was obtained by flowing the Ar-diluted mixture gas which contained certain concentration of CO, H₂, and O₂ at different flow rate. The sample loop of TCD-GC and FID-GC is 1 mL. The flow rate of the CO₂ gas in the system is 30 mL/min.