Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Z-scheme water splitting utilizing $CuLi_{1/3}Ti_{2/3}O_2$ as a hydrogen-evolving photocatalyst with photo-response up to 600 nm

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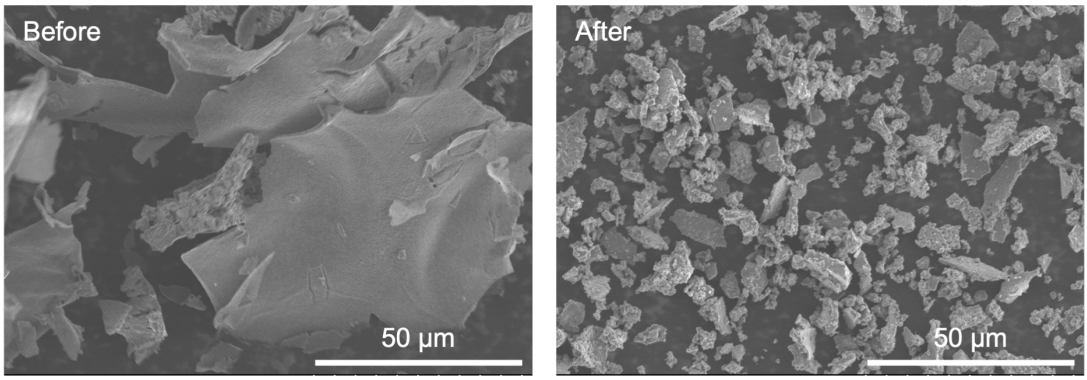

Fig. S1 SEM images of $Li_4Ti_5O_{12}$ before and after the pot-mill treatment.

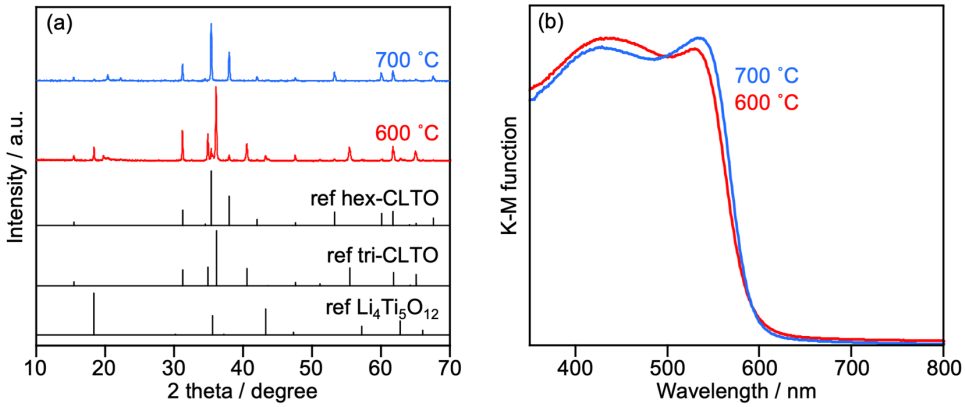

Fig. S2 (a) XRD patterns and (b) UV-vis spectra of CLTO prepared at 600 and 700 ºC. Reference patterns of hexagonal and trigonal CLTO were simulated from structure models of $CuGaO_2$ modified with composition and lattice constants of CLTO.

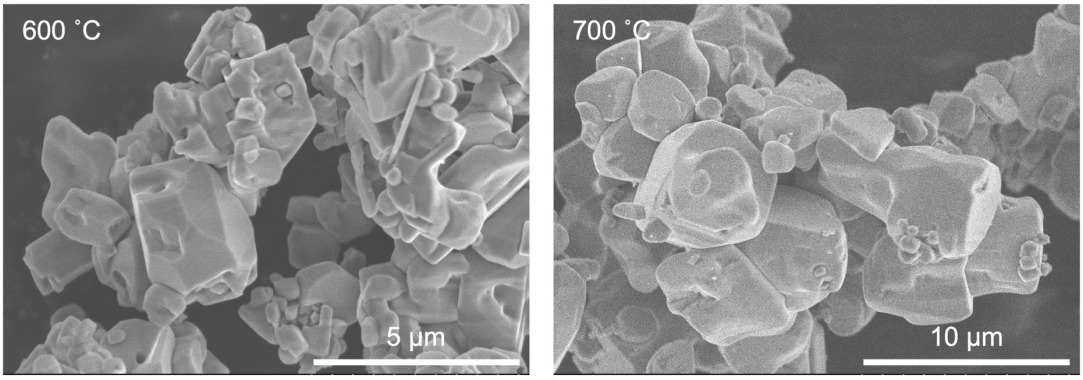

Fig. S3 SEM images of CLTO prepared at 600 and 700 ºC.

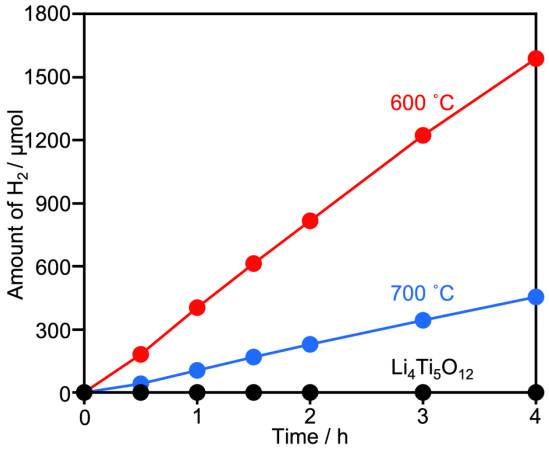

Fig. S4 Sacrificial H_2 evolution on Ru(0.5 wt%)/CLTO and $Li_4Ti_5O_{12}$ from an aqueous solution containing 0.1 M Na_2S and 0.5 M Na_2SO_3. Photocatalyst: 0.3 g; light source: 300 W Xe lamp ($\lambda > 420$ nm).

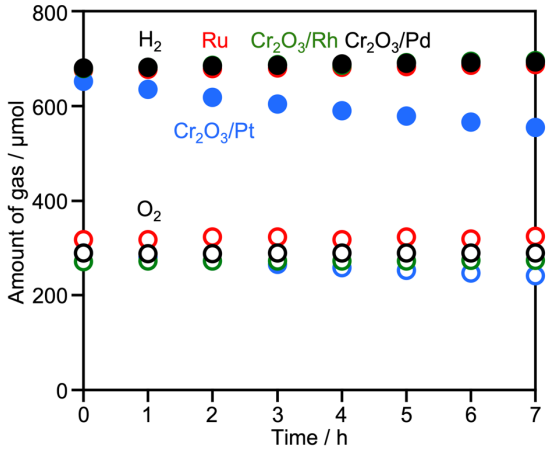

Fig. S5 Water formation over Ru/CLTO and Cr_2O_3/M/CLTO (M: Rh, Pd and Pt) in the dark. Catalyst: 0.05 g; H_2: 10 kPa; O_2: 5 kPa.

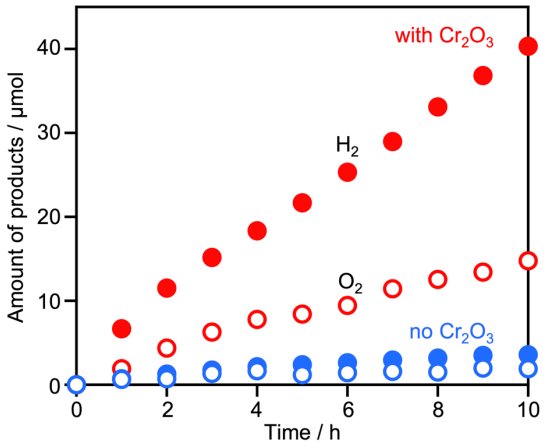

Fig. S6 Influences of Cr_2O_3 modification of Ru/CLTO upon Z-WS by Ru/CLTO-$BiVO_4$-$Co(bpy)_3SO_4$ system. Photocatalyst: 0.05 g each; reactant solution: 0.1 mM $Co(bpy)_3SO_4$, 160 mL; light source: 300 W Xe lamp ($\lambda > 420$ nm).

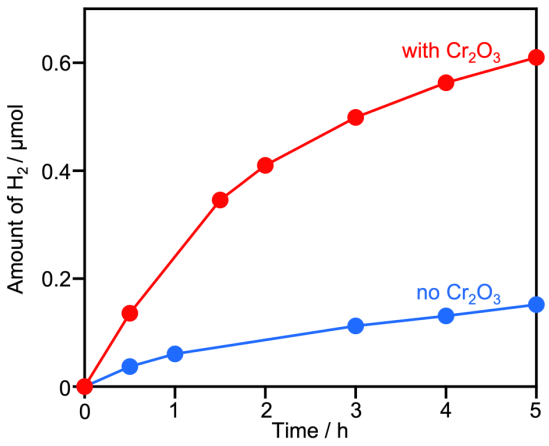

Fig. S7 Influences of Cr_2O_3 modification of Ru/CLTO upon H_2 evolution from a $Co(bpy)_3SO_4$ solution. Photocatalyst: 0.1 g; reactant solution: 0.5 mM $Co(bpy)_3SO_4$, 160 mL; light source: 300 W Xe lamp ($\lambda > 420$ nm).

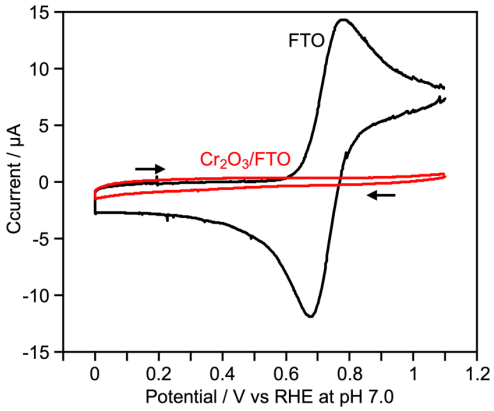

Fig S8. Current–potential curves of FTO and Cr_2O_3/FTO electrodes measured in a solution containing 0.1 M K_2SO_4 and 0.1 mM $Co(bpy)_3SO_4$ under Ar.

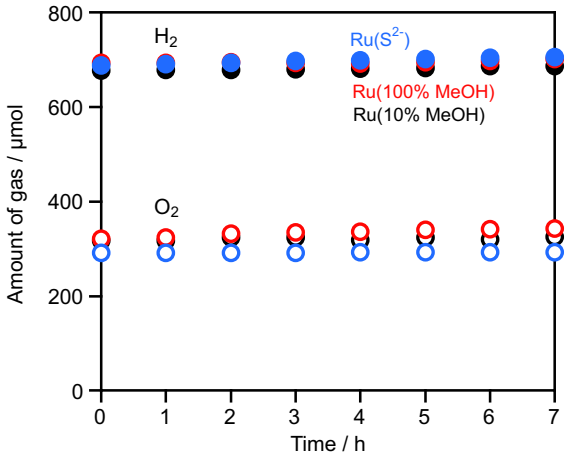

Fig. S9 Water formation over Ru/CLTO in the dark. Catalyst: 0.05 g; H_2: 10 kPa; O_2: 5 kPa.

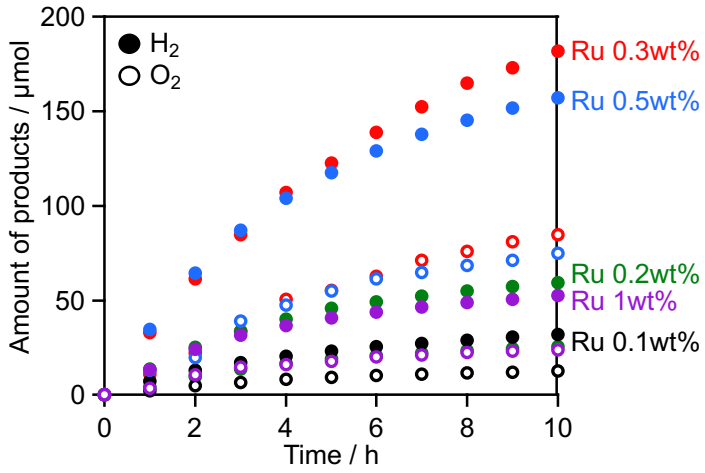

Fig. S10 Influences of Ru amounts upon Z-WS by the Cr_2O_3/Ru(100% MeOH)/CLTO-$BiVO_4$-$Co(bpy)_3SO_4$ system. Photocatalyst: 0.05 g each; reactant solution: 0.1 mM $Co(bpy)_3SO_4$, 160 mL; light source: 300 W Xe lamp ($\lambda > 420$ nm).

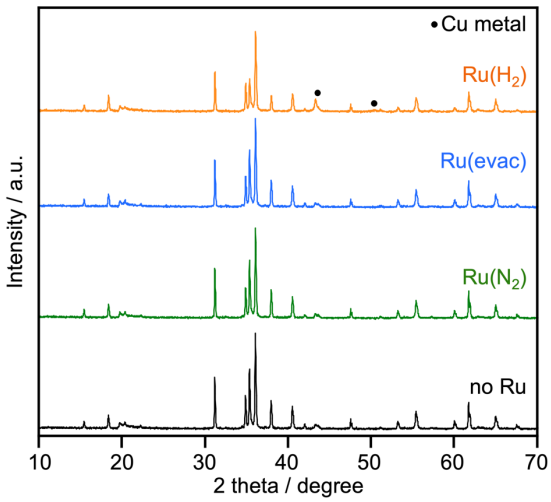

Fig. S11 XRD patterns of Ru/CLTO prepared by an impregnation method with different heat-treatment conditions.

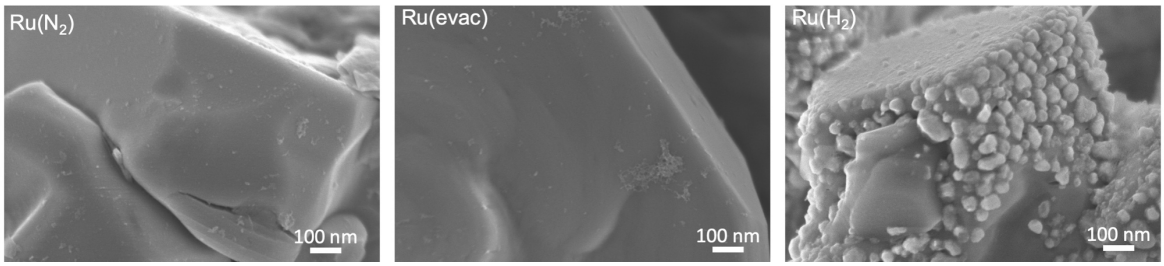

Fig. S12 SEM images of Ru/CLTO prepared by the impregnation method with different heat-treatment conditions.

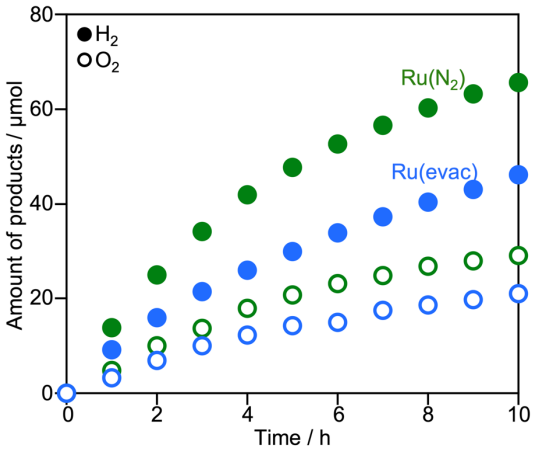

Fig. S13 Photocatalytic Z-WS using Cr_2O_3/Ru/CLTO prepared via the impregnation method with different heat treatment conditions. Photocatalyst: 0.05 g each; reactant solution: 0.1 mM $Co(bpy)_3SO_4$, 160 mL; light source: 300 W Xe lamp ($\lambda > 420$ nm).

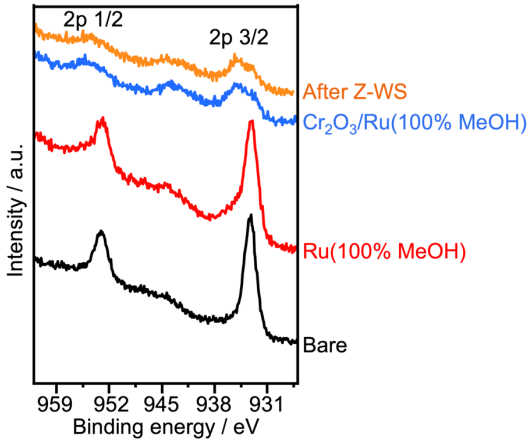

Fig. S14 XPS at Cu 2p of CLTO samples after photoirradiation including Z-WS.

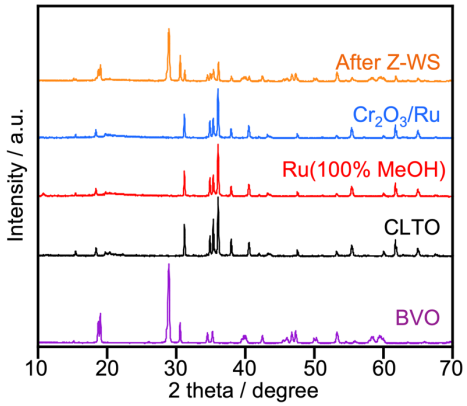

Fig. S15 XRD patterns of CLTO samples after photoirradiation including Z-WS.

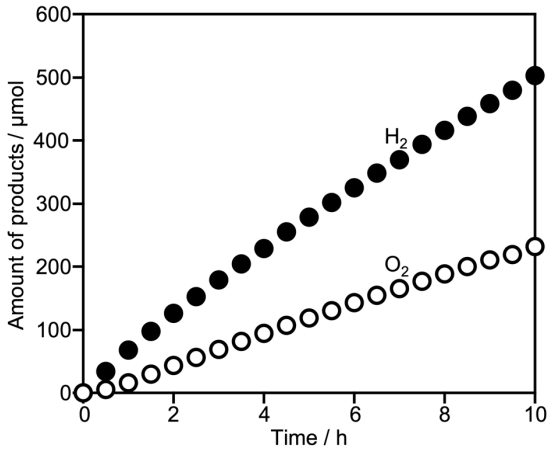

Fig. S16 Z-WS using the Ru/$SrTiO_3$:Rh-$BiVO_4$-$Co(bpy)_3SO_4$ system. Photocatalyst: 0.05 g each; reactant solution: 0.5 mM $Co(bpy)_3SO_4$, 160 mL; light source: 300 W Xe lamp ($\lambda > 420$ nm).

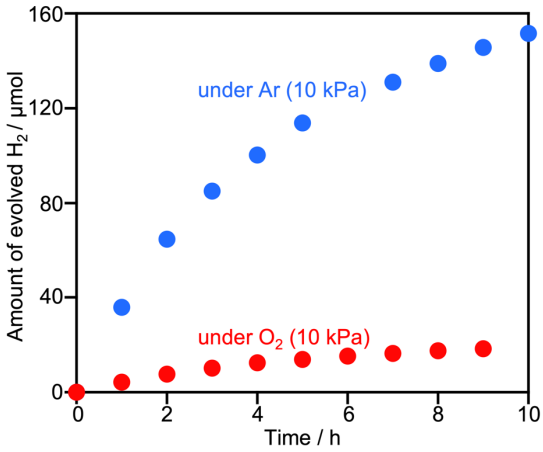

Fig. S17 Influence of O_2 upon H_2 evolution caused by water splitting using the Cr_2O_3/Ru/CLTO-$BiVO_4$-$Co(bpy)_3SO_4$ system. Photocatalyst: 0.05 g each; reactant solution: 0.1 mM $Co(bpy)_3SO_4$, 160 mL; light source: 300 W Xe lamp ($\lambda > 420$ nm). Only H_2 evolution is displayed because O_2 evolution was not detectable in the reaction under O_2 due to the quite large basic signal.