Supplementary information

Efficient light-driven CO₂ hydrogenation on Ru/CeO₂ catalysts

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Fig. S1 Photo images of the flow cell from the top view (a) and side view (b)

As for the loading of catalyst powder, quartz wool was used to block one side of the cuboid cavity, and catalyst powder was then added inside. After that, another side of the cuboid cavity was also blocked with quartz wool. The flow cell was then gently knocked until the catalyst powder vibrated to a uniform spreading.



Fig. S2 The distribution of diameters of Ru nanoparticles and the calculation of average size.



Fig. S3 EDS spectrum of Ru/CeO₂ sample.



Fig. S4 XPS analysis of Ru species of Ru/CeO_2 samples before and after H_2 reduction. The peaks at 284.8 eV are attributed to C 1s species arising from adventitious hydrocarbons.



Fig. S5 H₂-TPR profiles of Ru/CeO₂ catalysts after hydrogen pretreatment at 150 °C for 1 h.



Fig. S6 The relationship between illumination power and the resulted temperatures on the catalyst.



Fig. S7 CO_2 conversion over Ru/CeO₂ catalyst under "illumination" or "heating" model by the use of another reaction gas mixture (1% CO_2 , 5% H₂, and 94% Ar in volume).



Fig. S8 Typical GC spectra of the feed gas and output gas obtained over Ru/CeO_2 catalyst under illumination only (1.1 W cm⁻²).



Fig. S9 FTIR spectra recorded at 160 °C over the CeO₂ catalyst after injection of 0.1 ml pure CO₂ gas into the cell filled with Ar. The IR peaks at 2340 \sim 2360 cm⁻¹ are assigned to the signals from the gas-phase CO₂. And other peaks (peak locations are listed on the top of peaks) correspond to the adsorbed CO₂ species on the surface of CeO₂.



Fig. S10 Activation energies of hydrogen splitting on the surface of CeO_2 (a) and Ru (b)

The calculated results in Fig. S9 show that the hydrogen splitting on the surface of cerium oxide needs to overcome energy barrier of 2.27 eV, which is much higher than that on the surface of ruthenium (0.32 eV). This sharp contrast indicates that hydrogen molecules tend to be dissociated on ruthenium. Therefore, the ruthenium component of Ru/CeO₂ catalyst is responsible for hydrogen splitting in CO₂ hydrogenation process.



Fig. S11 CO₂ conversion over Ru/Al₂O₃ catalyst under "illumination" or "heating" model. In the synthesis procedure of Ru/Al₂O₃ catalyst, the loading of Ru nanocrystals was same as that of Ru/CeO₂ while commercial Al₂O₃ nanoparticles (Alfa Aesar, ~20 nm) were used as support material.