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Electronic Supplementary Information (ESI)

Selective dual-purpose photocatalysis for simultaneous H_2 evolution and mineralization of organic compound enabled by Cr_2O_3 barrier layer coated on $Rh/SrTiO_3$

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Experimental section

Preparation of photocatalysts

Cr_2O_3/Rh/$SrTiO_3$ photocatalyst was prepared by two-step photodeposition method similar to the reported method.[1] Rh was first photodeposited on $SrTiO_3$ (Aldrich, powder, 99%). Briefly, an aqueous suspension of $SrTiO_3$ (0.5 g) was irradiated with a 200 W mercury lamp for 30 min in the presence of Rh precursor ($RhCl_3$•$3H_2O$). Methanol (1 M, J. T. Baker) was added as an electron donor. The amount of Rh loading was fixed at 0.5 wt%. After the suspension was irradiated for 30 min, the Rh/$SrTiO_3$ powder was collected by filtration, washed with distilled water and dried overnight at 353 K. Cr_2O_3 was further deposited on Rh/$SrTiO_3$ using K_2CrO_4 as precursor. The loading amount of Cr_2O_3 was fixed at 0.75 wt%. The Rh/$SrTiO_3$ powder (250 mg) was dispersed in an aqueous K_2CrO_4 solution and was irradiated with a 200 W mercury lamp for 2 h without external electron donor in de-aerated condition to reduce K_2CrO_4 to Cr_2O_3.[1, 2] The final product was washed thoroughly with distilled water and dried overnight at 353 K. F-TiO_2/Pt photocatalyst was prepared as reported.[3] Pt was deposited on the surface of TiO_2 (Degussa P25) by the photocatalytic reduction of chloroplatinic acid (Pt content = 1.0 wt%) in the presence of methanol as an electron donor. For the fluorination of Pt/TiO_2 surface, 10 mM NaF was added into the aqueous suspension of Pt/TiO_2 and then pH was adjusted to the desired value.

Photocatalytic activity measurements

15 mg of catalyst powder was dispersed in distilled water (30 mL) by sonication for 60 seconds in an ultrasonic cleaning bath. Appropriate amount of the substrate stock solution was subsequently added to the suspension to give a desired initial concentration. The pH of the aqueous suspension was adjusted with concentrated NaOH or $HClO_4$ solution. The solution was purged by Ar gas for 1 h prior to irradiation while it was stirred in dark. The reactor was irradiated by a 300-W Xe arc lamp (Oriel). The light passed through a 10 cm IR filter and a UV cutoff filter ($\lambda \geq 320$ nm) under continuous stirring. The filtered was focused onto a 55 mL glass reactor (25 mL headspace) which was sealed with a rubber septum. The amount of evolved H_2 and O_2 in the headspace of the photocatalytic reactor was analyzed using gas chromatography (GC, HP6890A) equipped with a thermal conductivity detector. To determine the apparent photonic efficiency (APE) for H_2 production, the photocatalytic reaction experiments were also carried out under under irradiation of monochromated UV light from a Xe lamp (centered at $\lambda = 330$ nm). The incident photon flux was measured using a Power meter (Newport 1830-C) and then converted into an incident photon flux (I_{in}), which was estimated to be 1.33×10^{-3} Einstein h^{-1} assuming the monochromatic wavelength of 330 nm. APE of H_2 production was calculated by APE = 2 X [(number of H_2 molecules generated)/(number of incident photons)]. The concentration of 4-CP was measured using high performance liquid chromatography (HPLC, Agilent 1100 series) equipped with a diode array detector. The chloride ion (Cl^-) was analyzed using ion chromatography (IC, Dionex

DX-120) that was equipped with a conductivity detector and an AS-14 (4 mm X 250 mm) column. The total organic carbon (TOC) of organic substrates was measured using a TOC analyzer (TOC-VCSH, Shimadzu).

Photoelectrochemical tests

The measurement of photocurrent collected on an inert electrode (Pt) immersed in an aqueous suspension of catalyst were carried out with a three-electrode system similar to the previous report.[4] The $Fe^{3+/2+}$ redox couple was used as an electron shuttle which transfers the electrons from the photocatalyst particles to the Pt collector electrode in the continuously Ar purged system. A Pt wire, a Ag/AgCl electrode, and a graphite rod were used as a working, a reference, and a counter electrode, respectively. Photocatalyst suspension (1.0 g/L) with 0.5 mM Fe^{3+} (an electron shuttle) and 0.1 M $NaClO_4$ (electrolyte) at pH 3 was irradiated by a 300-W Xe arc lamp with a UV cutoff filter ($\lambda \geq 320$ nm). Photocurrent was collected in the suspension by applying a potential (+0.7 vs. Ag/AgCl) to the Pt working electrode using a potentiostat (Gamry, Reference 600)

References

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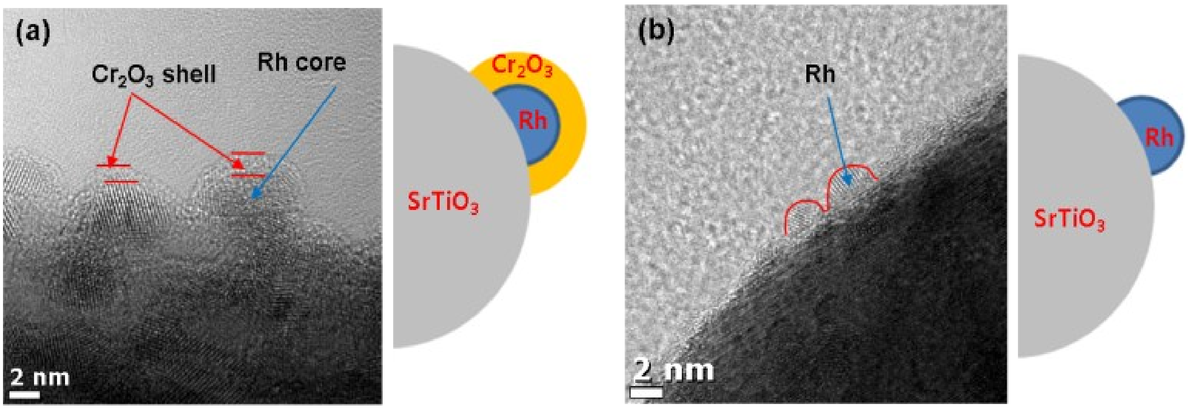

Fig. S1. HRTEM images of Cr_2O_3/Rh/$SrTiO_3$ and Rh/$SrTiO_3$.

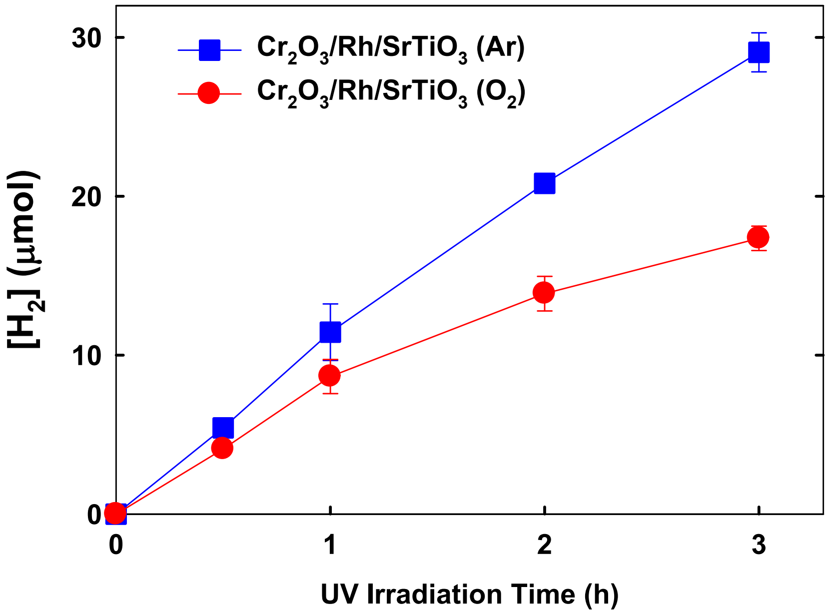

Fig. S2. Comparison of time profiles of H_2 production between Ar-saturated and air-saturated suspension of Cr_2O_3/Rh/$SrTiO_3$. Experimental conditions: [catalyst] = 0.5 g L^{-1}, $[4\text{-CP}]_0$ = 100 μM, $pH_0 = 7$, $\lambda > 320$ nm, air-tight, and initially Ar-purged for 1 h before UV irradiation.

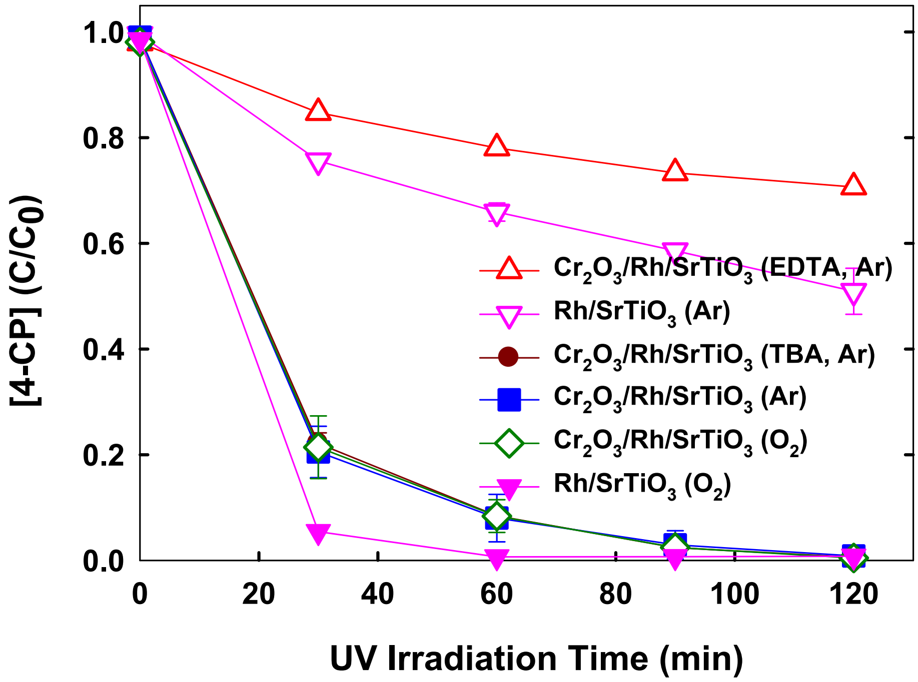

Fig. S3. Effects of dissolved O_2, TBA (OH radical scavenger), EDTA (hole scavenger) on the photocatalytic degradation of 4-CP in the suspensions of Cr_2O_3/Rh/$SrTiO_3$ and Rh/$SrTiO_3$.

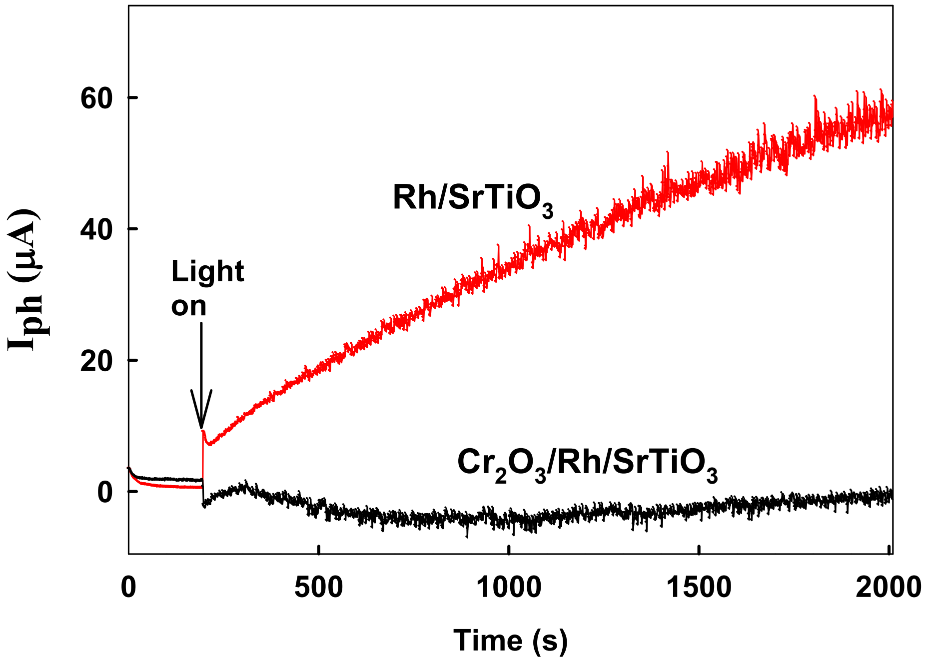

Fig. S4. Time profiles of Fe^{3+}-mediated photocurrent collected on a Pt electrode in UV light-irradiated suspension of photocatalysts.

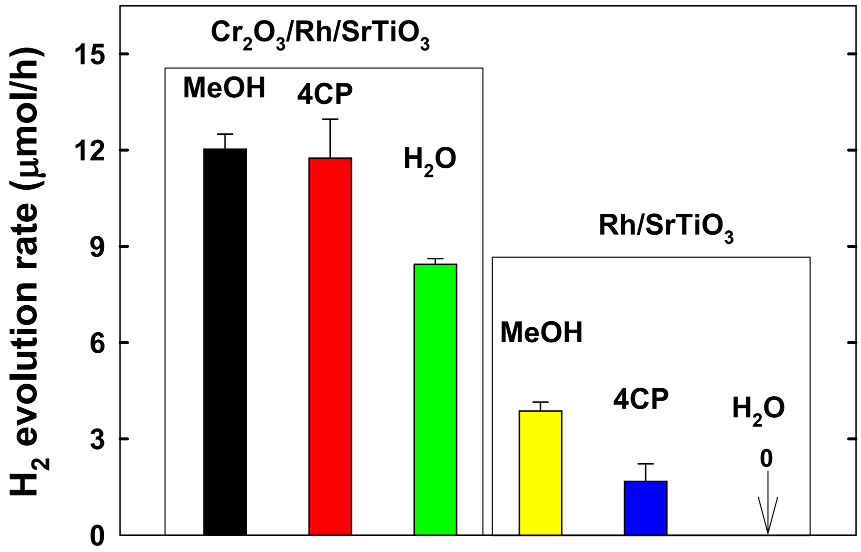

Fig. S5. Comparison of the H_2 production rates between Cr_2O_3/Rh/$SrTiO_3$ and Rh/$SrTiO_3$ photocatalytic systems with 4-CP (300 μM), MeOH (10 vol%), or no organic electron donor (H_2O) (at pH 7).. Experimental conditions: [catalyst] = 0.5 g/L, λ > 320 nm, air-tight and initially Ar-purged for 1 h before UV irradiation.

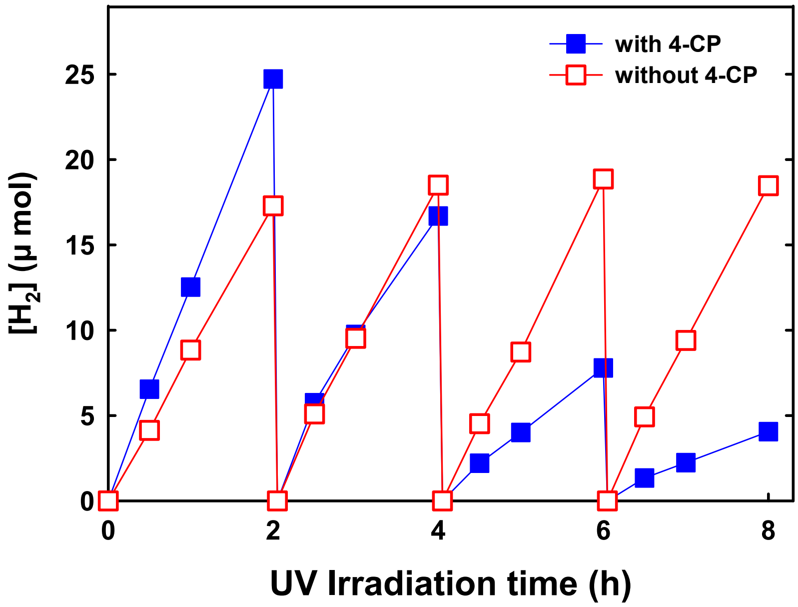

Fig. S6. Repeated cycle tests of Cr_2O_3/Rh/$SrTiO_3$ photocatalyst in the presence and absence of 4-CP. Experimental conditions: [catalyst] = 0.5 g L^{-1}, pH_0 = 7, λ > 320 nm, air-tight, injection of 100 μM 4-CP at the beginning of each cycle (for the case of "with 4-CP"), and initially Ar-purged for 1 h before UV irradiation and at the beginning of each cycle.

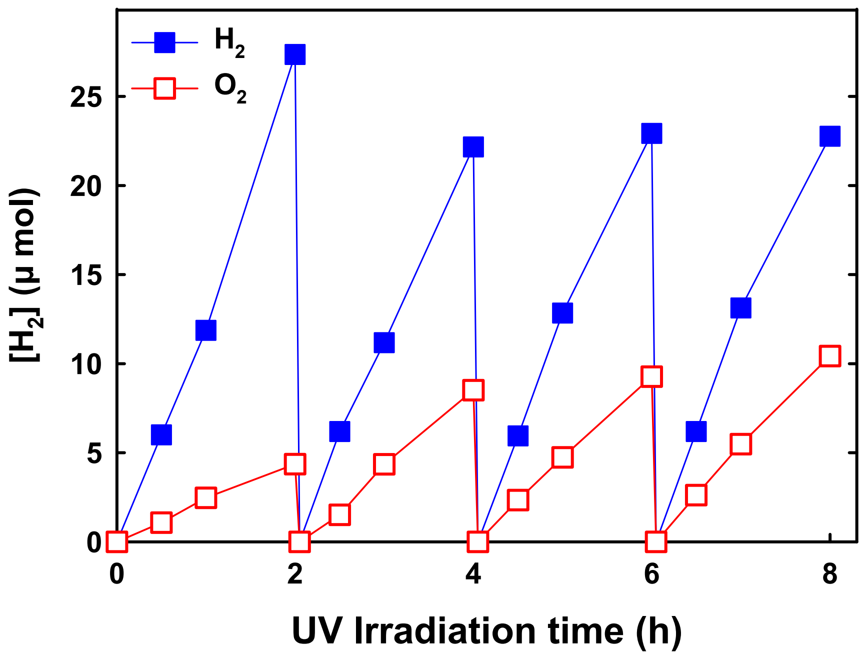

Fig. S7. Photocatalytic evolution of H2 and O2 during the repeated cycles. 4-CP (100 μM) was initially added before starting the first cycle and not replenished in the following cycles. At the end of each cycle, the suspension was purged with Ar. Experimental conditions: [catalyst] = 0.5 g/L, λ > 320 nm, air-tight and initially Ar-purged for 1 h before UV irradiation.