Supporting Information

Visible-Light-Responsive $CuLi_{1/3}Ti_{2/3}O_2$ Powders Prepared by a Molten CuCl Treatment of Li_2TiO_3 for Photocatalytic H_2 Evolution and Z-Schematic Water Splitting

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Photoelectrochemical measurement

$CuLi_{1/3}Ti_{2/3}O_2$ and TiO_2 electrodes were prepared by an electrophoretic method. 0.1 g of $CuLi_{1/3}Ti_{2/3}O_2$ or TiO_2 was dispersed in 20 mL of acetone (Kanto Chemical; 99.0%). Two FTO electrodes (AGC fabritech; < 12 Ω/□, 1.8 mm×10 mm×20 mm) were parallel immersed with distance of 1 cm in the suspension, and 60 V was applied between the two electrodes for 1–2 min using a direct-current power source (GPC-6030D; GW INSTEK). These electrodes calcined at 573 K for 2 h in N_2 for $CuLi_{1/3}Ti_{2/3}O_2$ and in air for TiO_2. Photoelectrochemical properties were evaluated using a potentiostat (Hokuto Denko; HZ-5000) and an H-type cell with Nafion 117 (Dupont). Platinum and Ag/AgCl with saturated KCl electrodes (DKK-TOA) were used as counter and reference electrodes, respectively. A buffered aqueous solution containing 0.1 mol L^{-1} of K_2SO_4 (Kanto Chemical; 99.0%), 0.025 mol L^{-1} of Na_2HPO_4 (Kanto Chemical; 99.5%), and 0.025 mol L^{-1} of KH_2PO_4 (Kanto Chemical; 99.6%) was used as an electrolyte at pH 6.9. The electrolytes in both compartments were bubbled with N_2 for deaeration before measurements. A 300 W Xe arc lamp (PerkinElmer; CERMAX PE300BF) with long-pass filters (HOYA), an NIR-absorbing filter (Sigma Koki; CCF-50S-500C) and a plano-convex lens (Sigma Koki; SLSQ- 60_150P) was used as a light source.

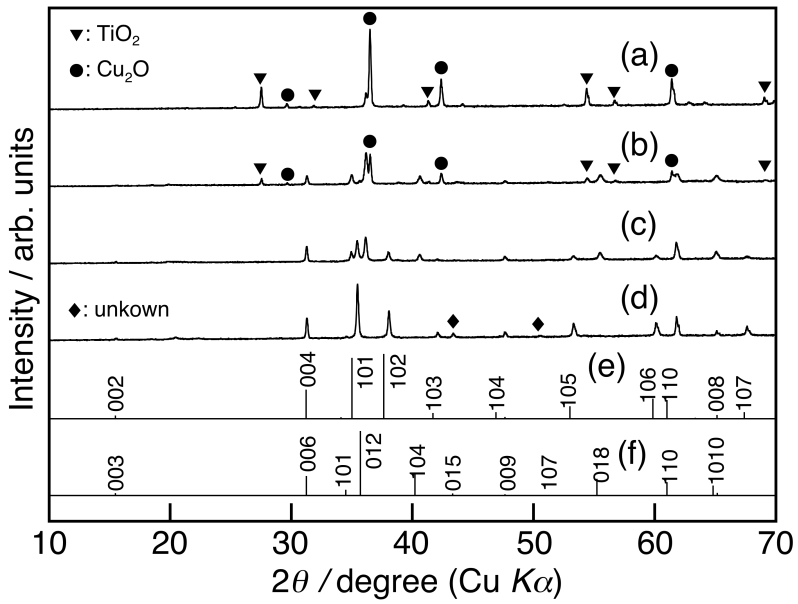

Figure S1 X-ray diffraction patterns of $CuLi_{1/3}Ti_{2/3}O_2$ prepared by a solid-state reaction at (a) 673, (b) 873, (c) 1073, and (d) 1273 K for 10 h, (e) hexagonal-$CuFeO_2$ (PDF: 1-75-2146), and (f) trigonal-$CuFeO_2$ (PDF: 1-75-2146).

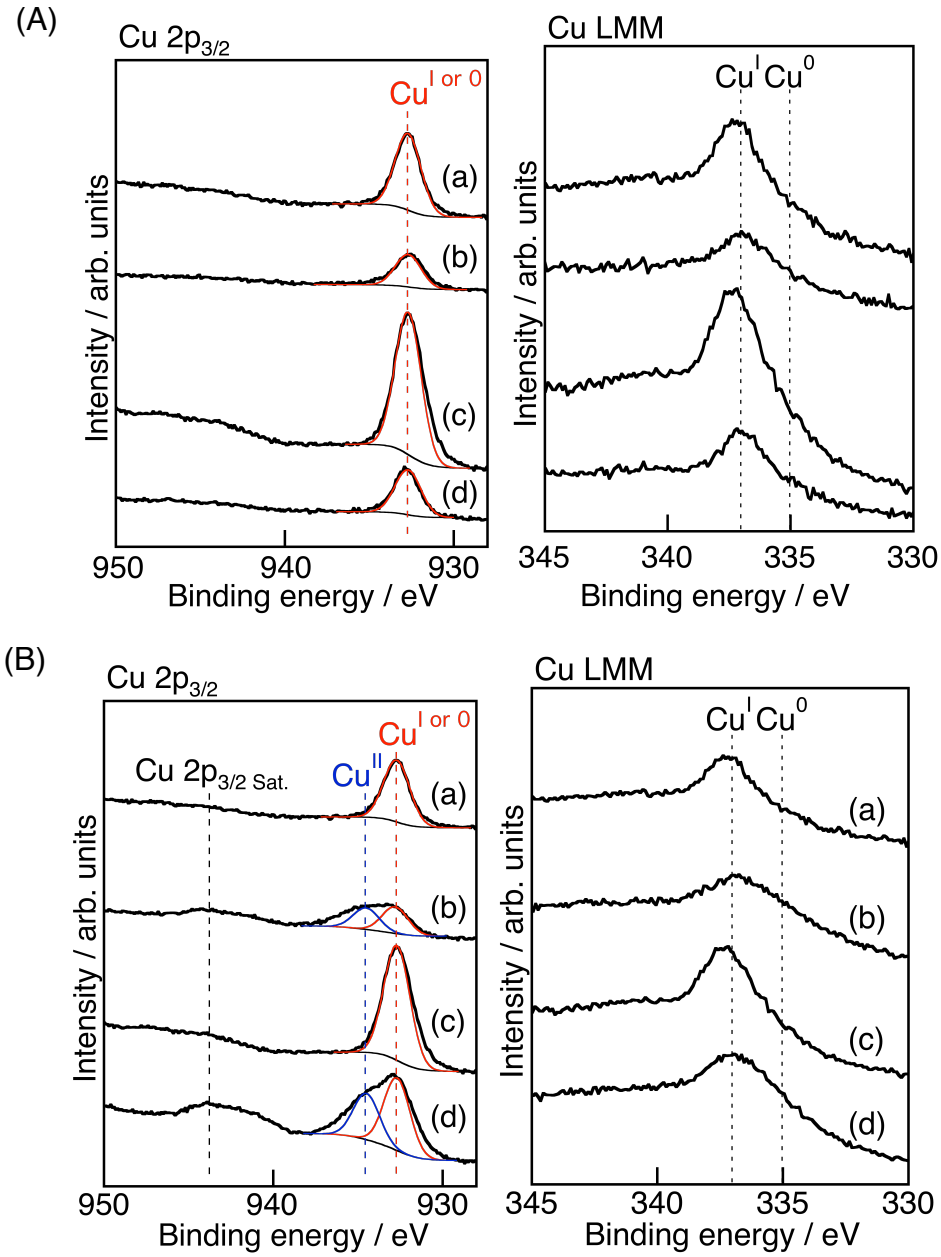

Figure S2 X-ray photoelectron spectra of (a, b) $CuLi_{1/3}Ti_{2/3}O_2$(hex) and (c, d) $CuLi_{1/3}Ti_{2/3}O_2$(tri) (a, c) before and (b, d) after photocatalytic H_2 evolution from aqueous (A) 0.5 mol L^{-1} K_2SO_3 + 0.1 mol L^{-1} Na_2S and (B) methanol (pH 10, using $NaOH_{aq.}$) solutions. $CuLi_{1/3}Ti_{2/3}O_2$(hex) and $CuLi_{1/3}Ti_{2/3}O_2$(tri) were prepared by treating Li_2TiO_3(cub) at 873 K and Li_2TiO_3(mon) at 773 K with a molten CuCl, respectively.

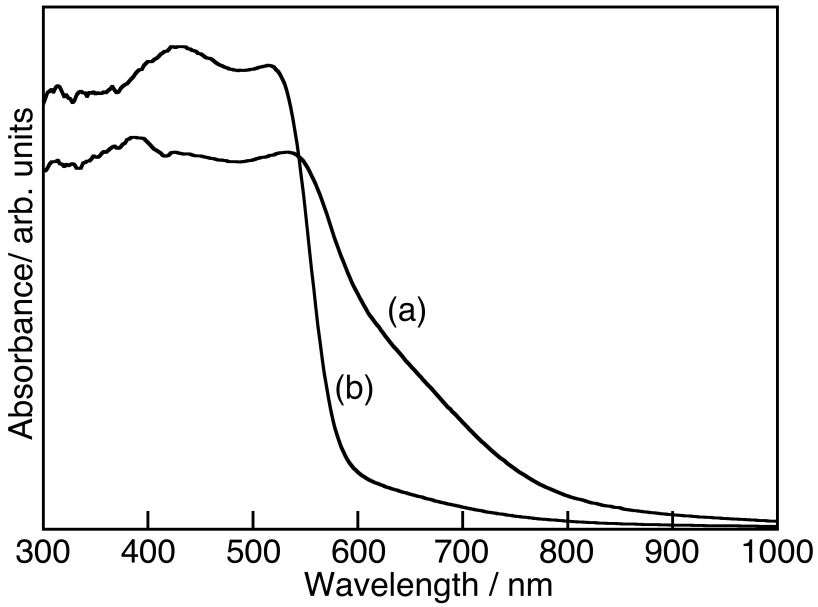

Figure S3 Diffuse reflectance spectra of hexagonal-$CuLi_{1/3}Ti_{2/3}O_2$ (a) obtained from $CuLi_{1/3}Ti_{2/3}O_2$(tri) by calcination at 1273 K for 2 h in N_2 and (b) prepared by a solid-state reaction at 1273 K for 10 h.

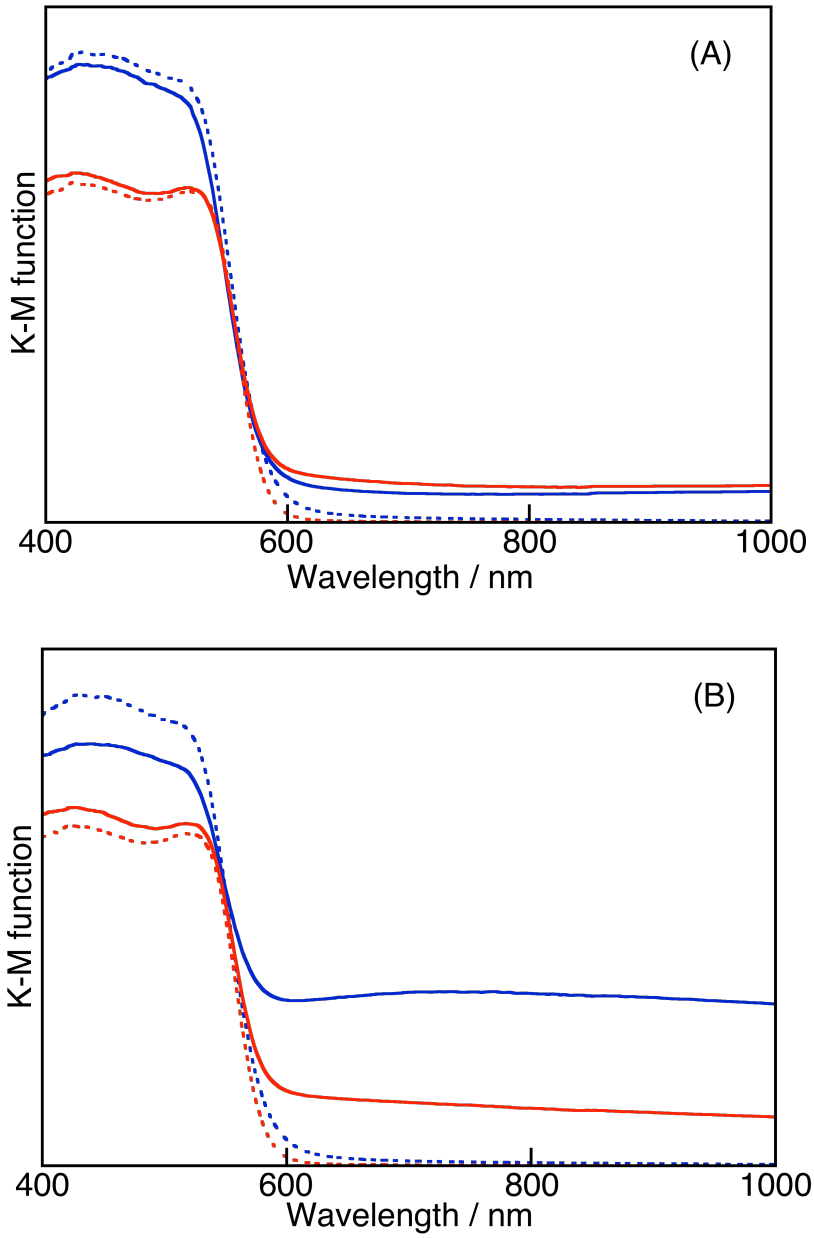

Figure S4 Diffuse reflectance spectra of (red lines) $CuLi_{1/3}Ti_{2/3}O_2$(hex) and (blue lines) $CuLi_{1/3}Ti_{2/3}O_2$(tri) (dotted lines) before and (solid lines) after photocatalytic H_2 evolution from aqueous (A) 0.5 mol L^{-1} K_2SO_3 + 0.1 mol L^{-1} Na_2S and (B) methanol (pH 10, using $NaOH_{aq.}$) solutions.

$CuLi_{1/3}Ti_{2/3}O_2$(hex) and $CuLi_{1/3}Ti_{2/3}O_2$(tri) were prepared by treating Li_2TiO_3(cub) at 873 K and Li_2TiO_3(mon) at 773 K with a molten CuCl, respectively.

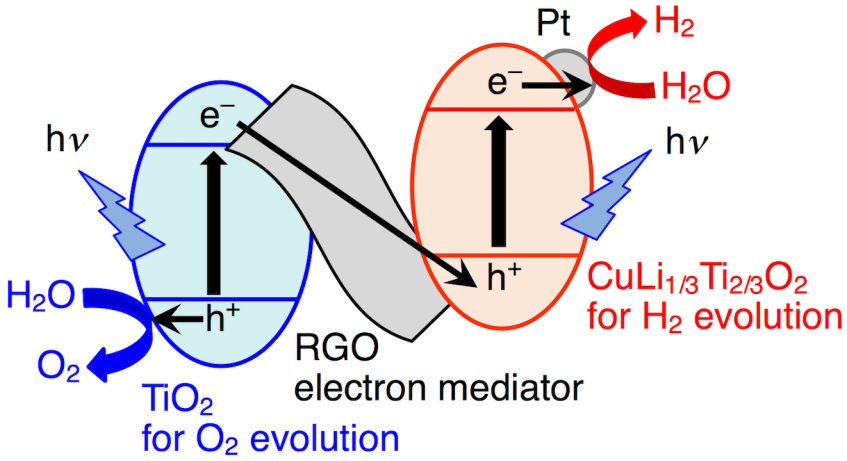

Figure S5 An illustration of a constructed Z-scheme system consisting of Pt/$CuLi_{1/3}Ti_{2/3}O_2$, TiO_2, and an RGO electron mediator.

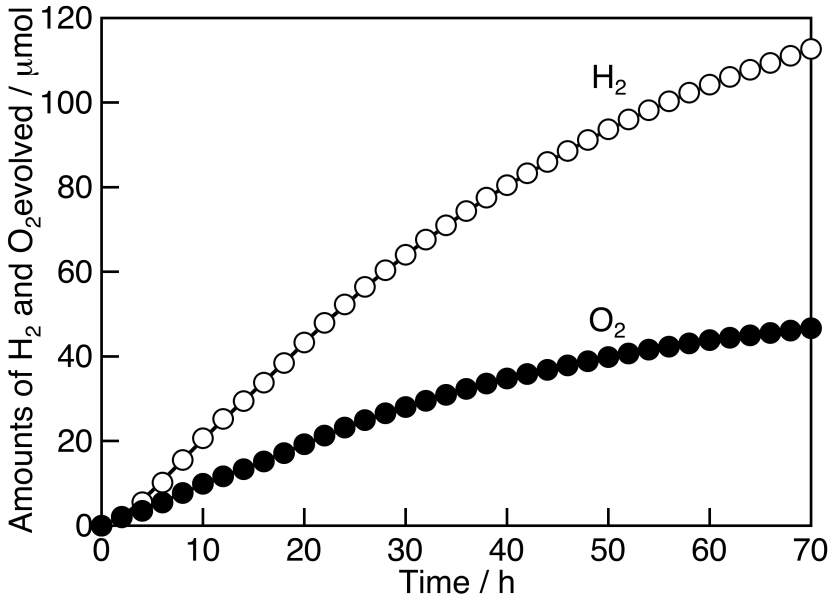

Figure S6 Z-schematic water splitting using Pt(0.3 wt%)-loaded $CuLi_{1/3}Ti_{2/3}O_2$(hex) and RGO-TiO_2 composite.

Catalyst: 0.05 g each, solution: water without pH adjustment (120 mL), light source: 300 W Xe lamp, cell: top-irradiation cell with a Pyrex window.

$CuLi_{1/3}Ti_{2/3}O_2$(hex) was prepared by treating Li_2TiO_3(cub) at 873 K with a molten CuCl.

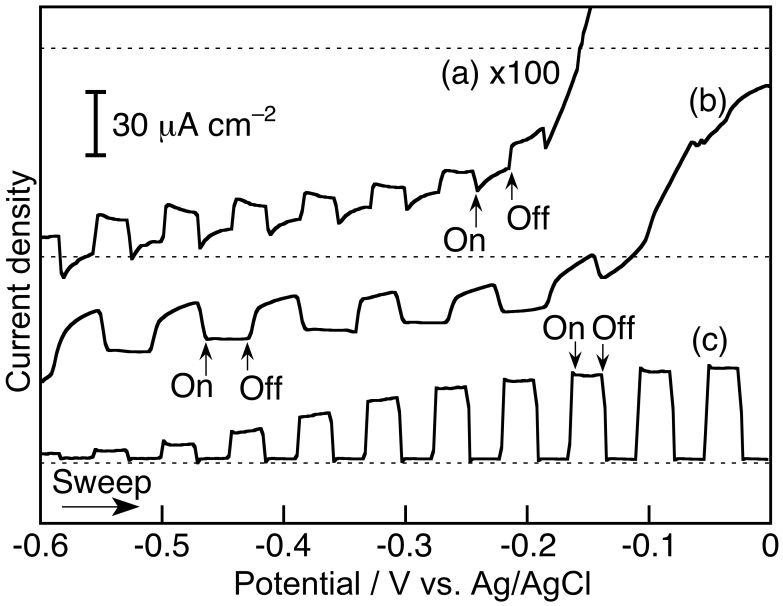

Figure S7 Current vs. potential curves of (a) $CuLi_{1/3}Ti_{2/3}O_2$(hex), (b) $CuLi_{1/3}Ti_{2/3}O_2$(tri), and (c) TiO_2 photoelectrodes. (a, b) $\lambda > 420$ nm and (c) $\lambda > 300$ nm. Electrolyte: 0.1 mol L^{-1} $K_2SO_{4\ aq.}$ + 0.05 mol L^{-1} $KH_2PO_{4\ aq.}$ + 0.05 mol L^{-1} $NaH_2PO_{4\ aq.}$ (pH 6.8), sweep rate: 20 mV s^{-1}, light source: 300 W Xe lamp. Dashed line showed 0 A for each electrode. $CuLi_{1/3}Ti_{2/3}O_2$(hex) and $CuLi_{1/3}Ti_{2/3}O_2$(tri) were prepared by treating Li_2TiO_3(cub) at 873 K and Li_2TiO_3(mon) at 773 K with a molten CuCl, respectively.