## Effect of Particle Size of La<sub>5</sub>Ti<sub>2</sub>CuS<sub>5</sub>O<sub>7</sub> on Photoelectrochemical Properties in Solar Hydrogen Evolution

Jingyuan Liu,<sup>a</sup> Takashi Hisatomi,<sup>a</sup> Masao Katayama,<sup>a</sup> Tsutomu Minegishi,<sup>a,b</sup> Jun Kubota,<sup>a,†</sup> and Kazunari Domen<sup>a,\*</sup>

<sup>a</sup> Department of Chemical System Engineering, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, 113-8656 Tokyo, Japan

<sup>b</sup> Japan Science and Technology Agency / Precursory Research for Embryonic Science and Technology (JST/PRESTO), Kawaguchi Center Building, 4-1-8, Honcho, Kawaguchi-shi, 332-0012 Saitama, Japan

<sup>†</sup>Current Affiliation: Department of Chemical Engineering, Fukuoka University 8-19-1 Nanakuma, Jonan-ku, 814-0180 Fukuoka, Japan



**Figure S1.** XRD patterns for (a) the reference LTC (ICSD #99612),<sup>S1</sup> (b) undoped, (c) Sc-doped, (d) Mg-doped, and (e) Al-doped LTC.



Figure S2. SEM images for (a) undoped, (b) Sc-doped (c) Mg-doped, and (d) Aldoped LTC.



Figure S3. DRS for (a) undoped, (b) Sc-doped (c) Mg-doped, and (d) Al-doped LTC.



**Figure S4.** Current-potential curves for (a) undoped, (b) Sc-doped, (c) Mg-doped, and (d) Al-doped LTC photocathodes under chopped simulated sunlight illumination.



**Figure S5.** Current-potential curves for photocathodes of Mg-doped LTC powders synthesized with annealing durations of (a) 48 and (b) 96 h. The measurements were carried out in a 0.1 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution (pH 10) under chopped simulated sunlight irradiation. The photocathodes were modified with Pt by photodeposition.



**Figure S6.** Time courses of hydrogen and oxygen evolution using a Mg-doped LTC photocathode (annealed for 96 h; projected area 2.0 cm<sup>2</sup>) in a three-electrode configuration under visible light irradiation ( $\lambda > 420$  nm) by a 300 W Xe lamp equipped with a 420 nm long-pass cutoff filter and a dichroic mirror. The electrode potentials employed were 0 (left panel) and 0.65 V (right panel) vs. RHE. The solid

curves labelled e<sup>-</sup>/2 and e<sup>-</sup>/4 show the numbers of hydrogen and oxygen molecules that are generated at unity faradaic efficiency, respectively. The measurements were carried out in 0.1 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution adjusted to pH 10.



**Figure S7.** Normalized IPCE spectra of (a,b) large-sized Mg-doped LTC measured at (a) 0 and (b) 0.65 V vs. RHE and (c,d) small-sized Mg-doped LTC measured at (c) 0 and (d) 0.65 V vs. RHE in  $Na_2SO_4$  aqueous solution adjusted to pH 10. The photocathodes were modified with Pt by photodeposition.

## Reference

S1. V. Meignen, L. Cario, A. Lafond, Y. Moëlo, C. Guillot-Deudon, A. Meerschaut, J. Solid State Chem., 2004, **177**, 2810.