Supporting Information

**Title:** Investigation of the enhanced photocathodic activity of La$_5$Ti$_2$CuS$_5$O$_7$

photocathodes in H$_2$ evolution by synchrotron radiation nanospectroscopy.

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**Figure S1.** $I$–$E$ curves for undoped LTC and Ga-doped LTC photocathodes under simulated AM1.5G light. A 0.1 M Na$_2$SO$_4$ aqueous solution adjusted to pH 10 by adding NaOH was used as the electrolyte.
Figure S2. La 4d XPS spectra for undoped and Ga-doped LTC with the peak fitting components. Open red circles represent the raw data and a black solid line is fitted data. The blue and green solid lines represent La 4d$_{5/2}$ and 4d$_{3/2}$ fitting components, respectively. Both La 4d$_{5/2}$ and 4d$_{3/2}$ peaks are fitted with three components, which is consistent with a previous report$^1$. The La 4d$_{5/2}$ peak of Ga-doped LTC shift to the lower binding energy by 0.36±0.05 eV compared to that of undoped LTC.
Figure S3. Valence band leading edge of LTC (lower) and Ga-doped LTC (upper). The VBMs of them are determined by the linear extrapolating method.
Figure S4. C1s and Au 4f XPS spectra with focused x-ray at a position of LTC surface. The kinetic energy at Fermi level is estimated as 998.0±0.1 eV from both C1s and Au 4f\textsubscript{7/2} peak position, which are assumed as 284.6 and 84.0 eV, respectively.
Supplementary References