

Supporting Information

Title: Investigation of the enhanced photocathodic activity of $\text{La}_5\text{Ti}_2\text{CuS}_5\text{O}_7$ photocathodes in H_2 evolution by synchrotron radiation nanospectroscopy.

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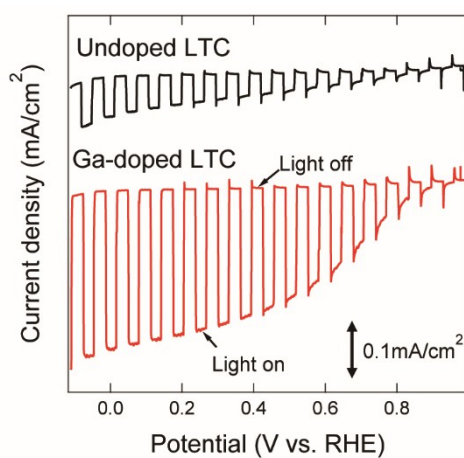


Figure S1. I - E curves for undoped LTC and Ga-doped LTC photocathodes under simulated AM1.5G light. A 0.1 M Na_2SO_4 aqueous solution adjusted to pH 10 by adding NaOH was used as the electrolyte.

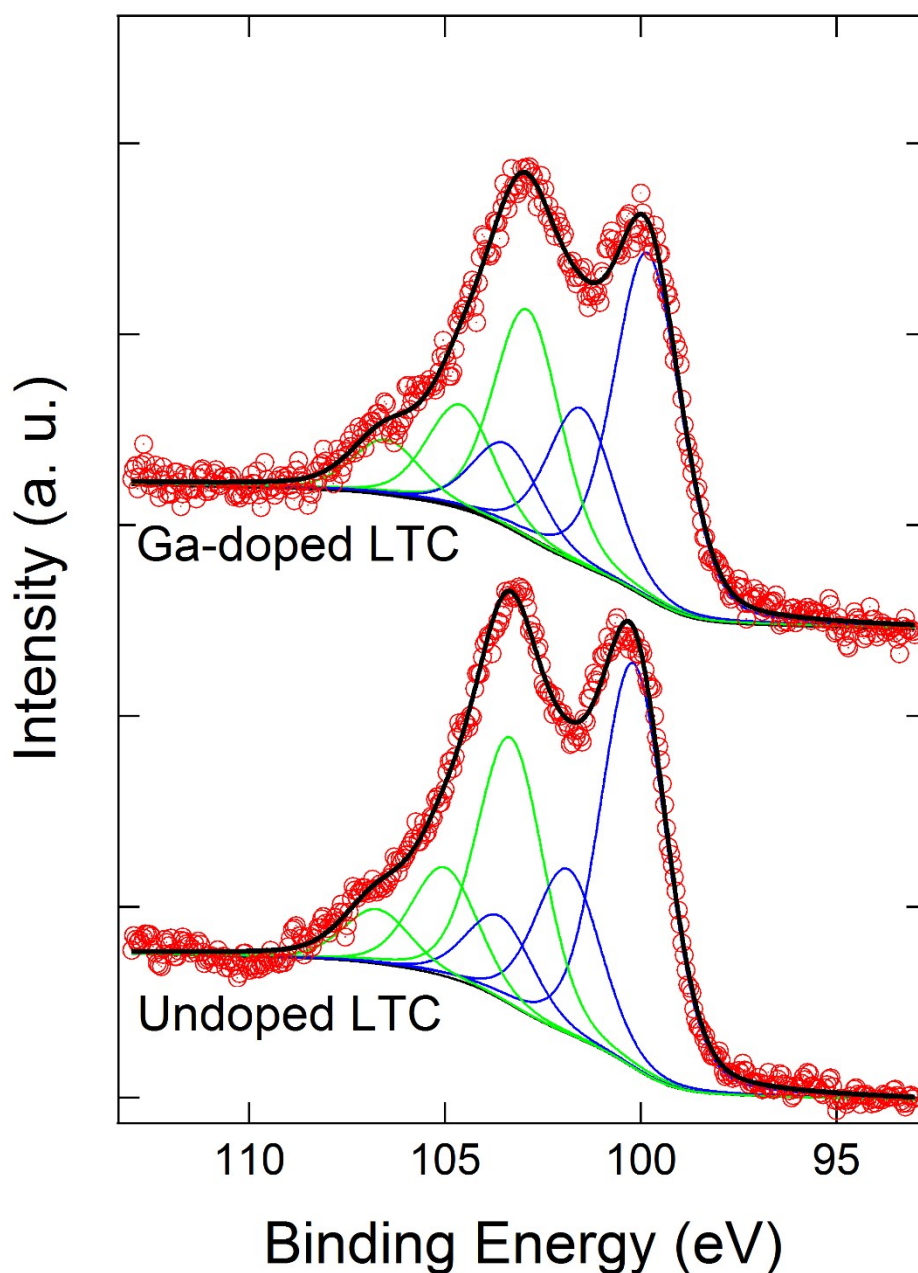


Figure S2. La 4d XPS spectra for undoped and Ga-doped LTC with the peak fitting components. Open red circles represent the raw data and a black solid line is fitted data. The blue and green solid lines represent La 4d_{5/2} and 4d_{3/2} fitting components, respectively. Both La 4d_{5/2} and 4d_{3/2} peaks are fitted with three components, which is consistent with a previous report¹. 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.

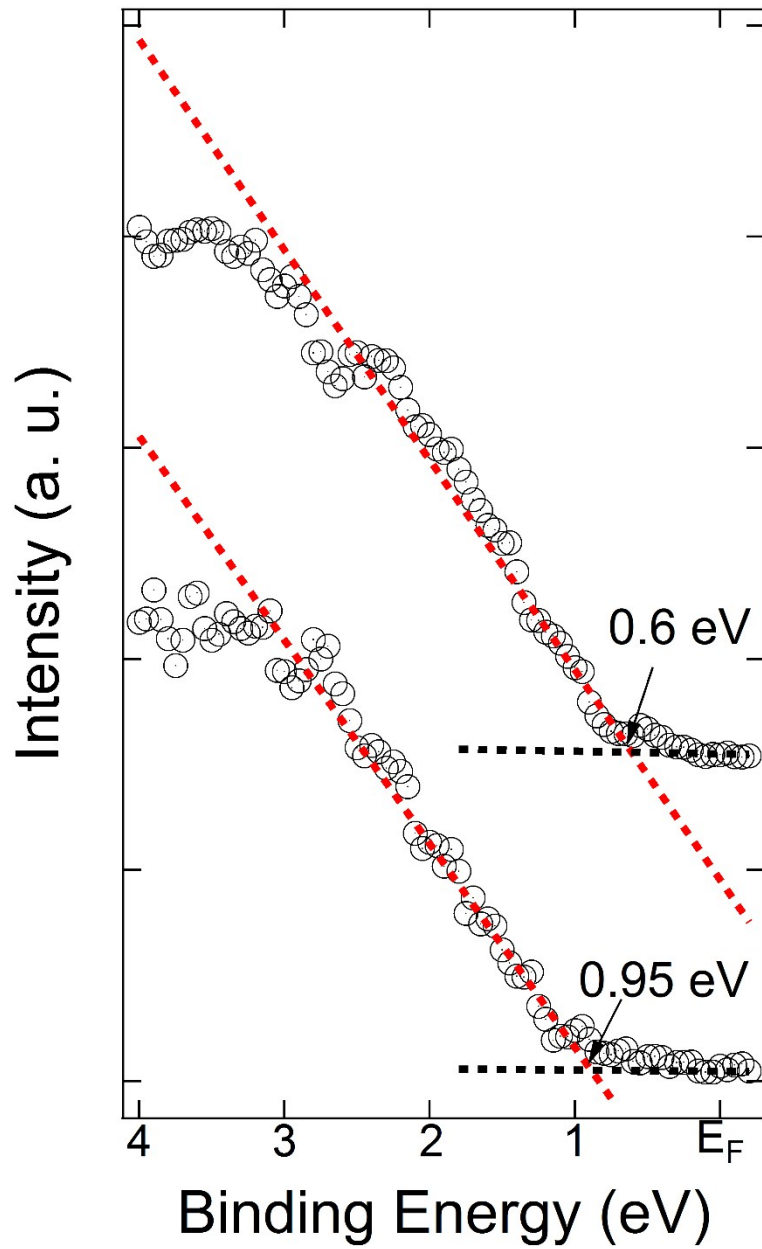


Figure S3. Valence band leading edge of LTC (lower) and Ga-doped LTC (upper). The VBMs of them are determined by the linear extrapolating method.

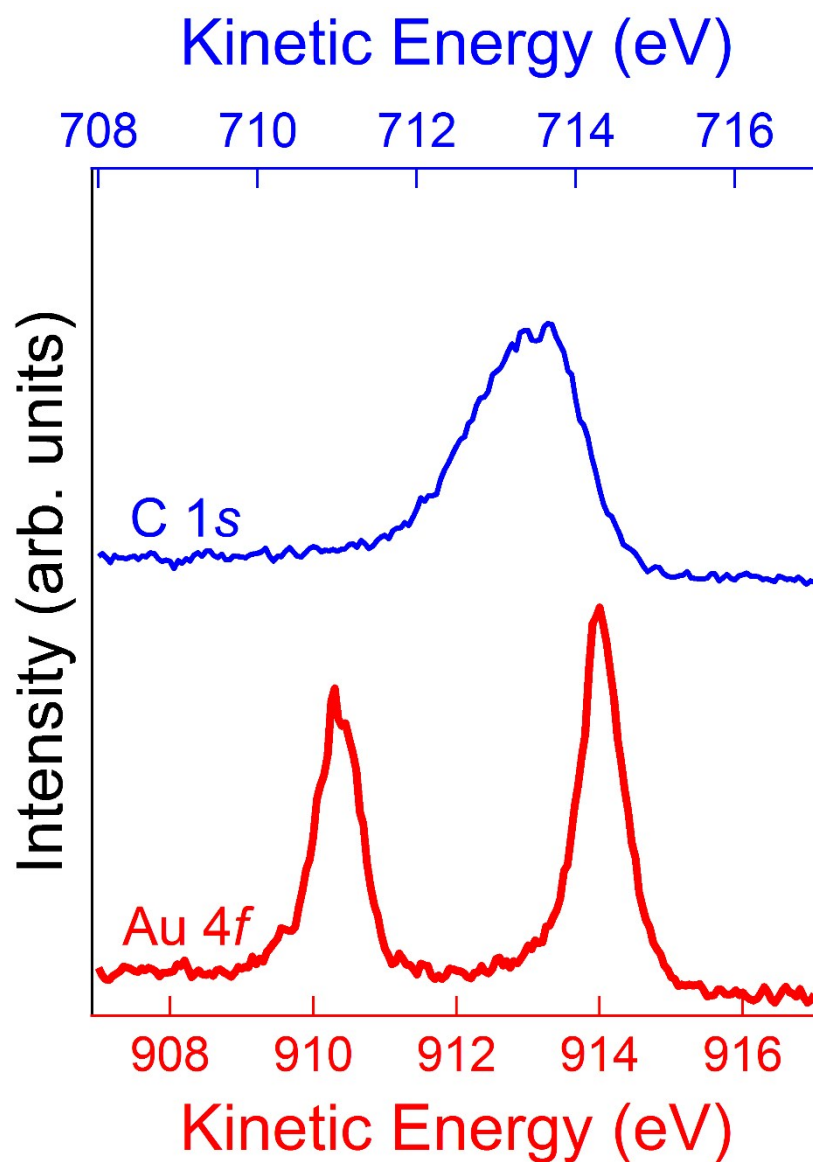


Figure S4. C1s and Au 4f XPS spectra with focused x-ray at a position of LTC surface. The kinetic energy at Fermi level is estimated as 998.0 ± 0.1 eV from both C1s and Au $4f_{7/2}$ peak position, which are assumed as 284.6 and 84.0 eV, respectively.

Supplementary References

1. M. F. Sunding, K. Hadidi, S. Diplas, O. M. Løvvik, T. E. Norby and A. E. Gunnæs, *J. Electron Spectros. Relat. Phenomena*, 2011, **184**, 399–409.