

## Supporting Information

# Binary flux-promoted formation of trigonal ZnIn<sub>2</sub>S<sub>4</sub> layered crystals using ZnS-containing industrial waste and their photocatalytic performance for H<sub>2</sub> production†

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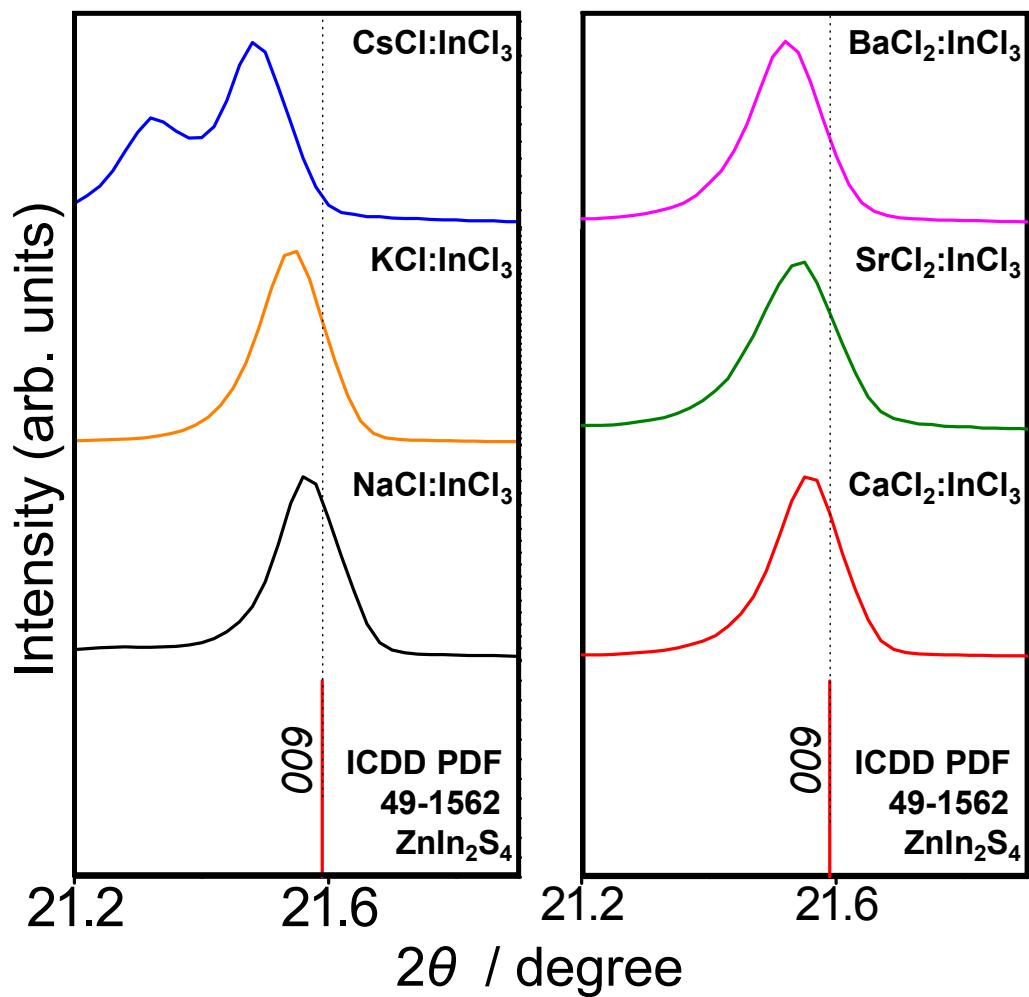
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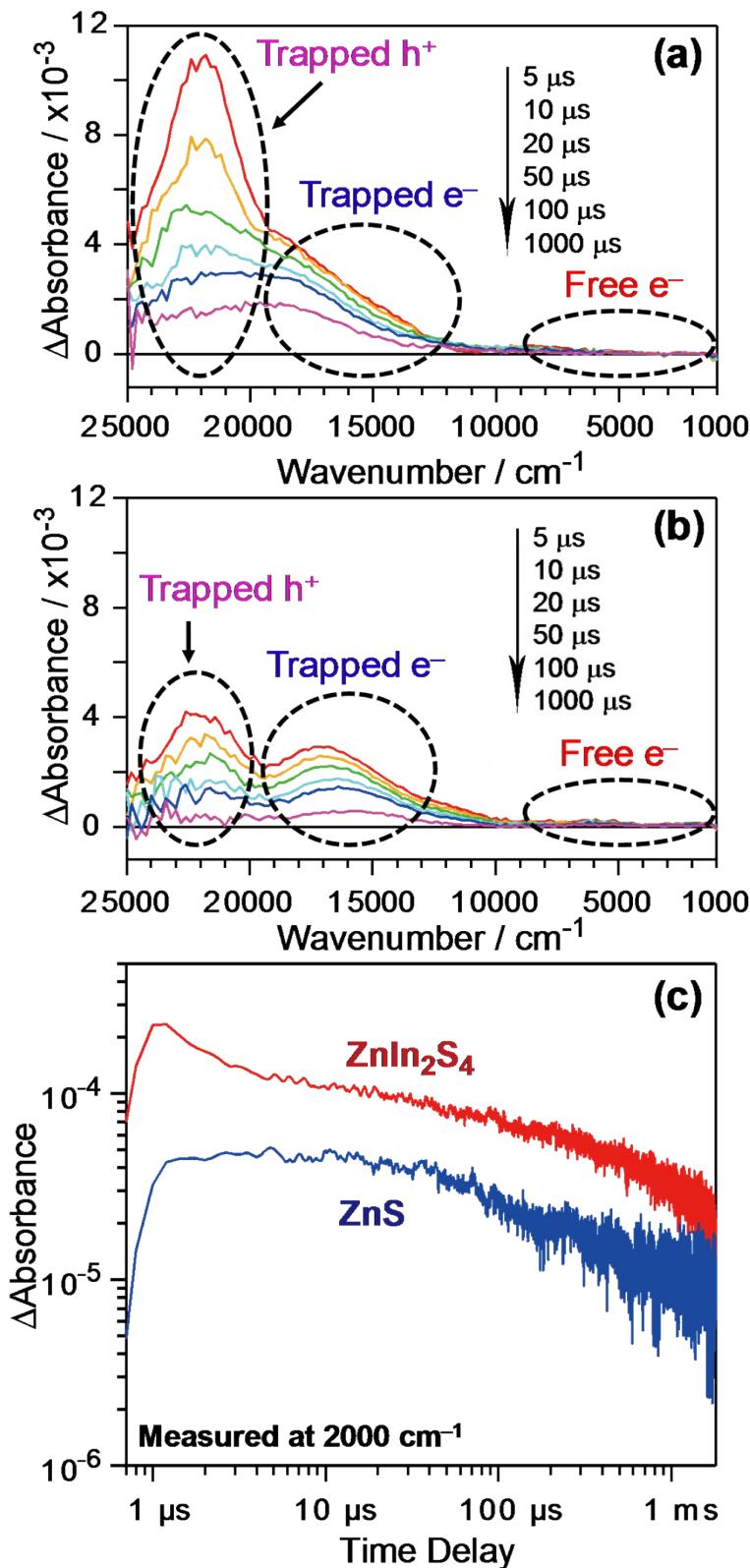
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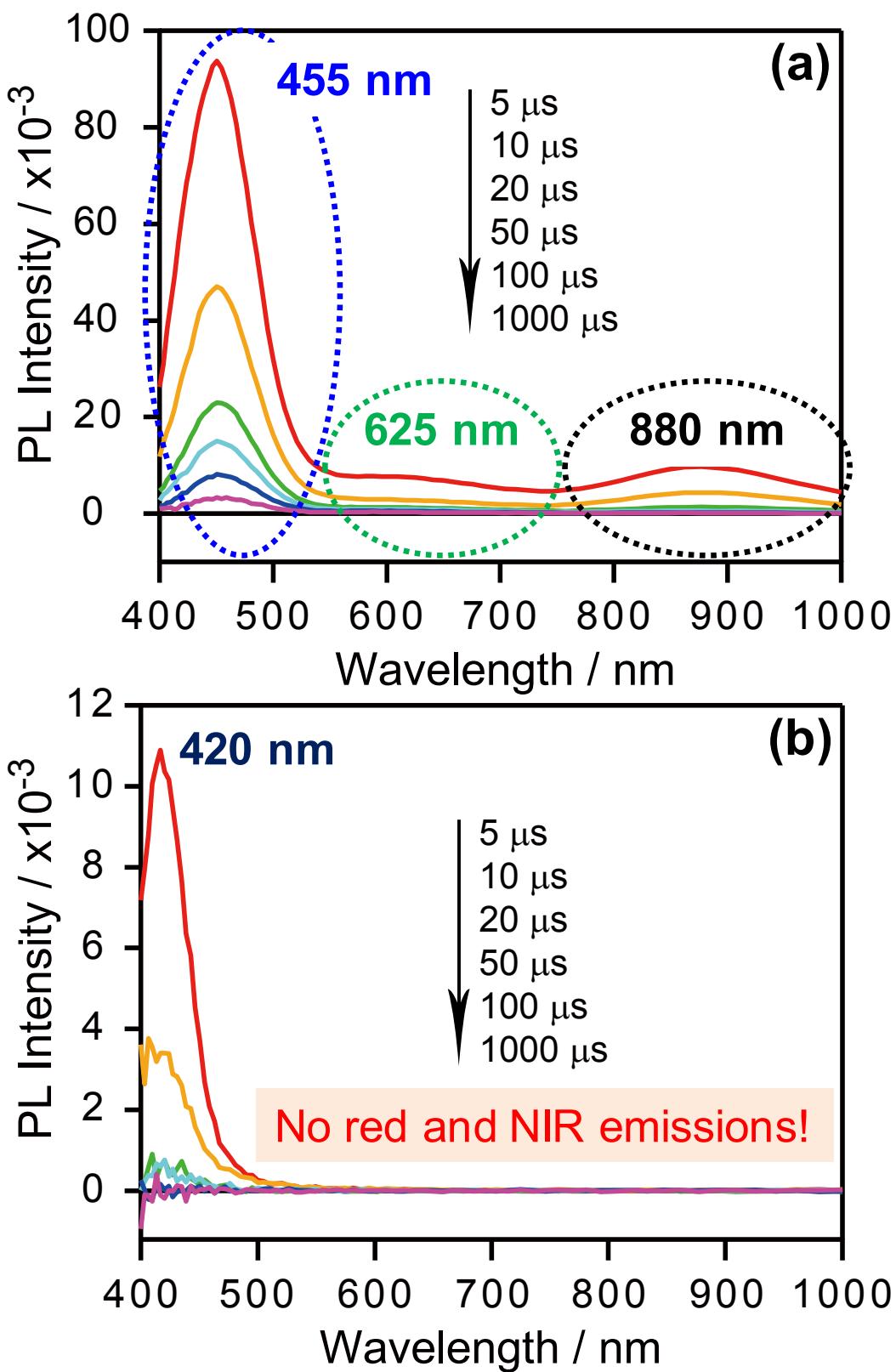
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**Figure S1.** Enlarged XRD patterns of  $\text{ZnIn}_2\text{S}_4$  crystals grown by a flux method at 800°C for 1 h under  $\text{N}_2$  atmosphere with a 40 mol% solute concentration using different fluxes:  $\text{NaCl:InCl}_3$ ,  $\text{KCl:InCl}_3$ ,  $\text{CsCl:InCl}_3$ ,  $\text{CaCl}_2:\text{InCl}_3$ ,  $\text{SrCl}_2:\text{InCl}_3$ , and  $\text{BaCl}_2:\text{InCl}_3$ .



**Figure S2.** Transient absorption spectra of (a) ZnS and (b)  $\text{ZnIn}_2\text{S}_4$  crystals grown by a flux method using KCl:InCl<sub>3</sub> flux excited by UV laser pulses (355 nm, 6-ns duration, 0.5 mJ per pulse, and 5 Hz) in nitrogen atmosphere. (c) Decay kinetics of photogenerated free electrons ( $2,000 \text{ cm}^{-1}$ ) in ZnS and  $\text{ZnIn}_2\text{S}_4$  crystals grown by a flux method using KCl:InCl<sub>3</sub> flux excited by UV laser pulses.



**Figure S3.** PL spectra of (a) ZnS and (b)  $\text{ZnIn}_2\text{S}_4$  crystals grown by a flux method using  $\text{KCl}:\text{InCl}_3$  flux.