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# Co-doping of a $La_5Ti_2Cu_{0.9}Ag_{0.1}O_7S_5$ photocatalyst ($\lambda < 700$ nm) with Ga and Al to enhance photocatalytic $H_2$ evolution

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## Text S1 Experimental details

### S 1.1 Preparation of LTCA

$La_2O_3$ (99.99%, Kanto Chemical Co., Inc.), $La_2S_3$ (99.9%, Kojundo Chemical Laboratory Co., Ltd.). $TiO_2$ (rutile, 99.99%, Rare Metallic Co., Ltd.), $Cu_2S$ (99%, Kojundo Chemical Laboratory Co., Ltd.), $Ag_2S$ (99%, Kojundo Chemical Laboratory Co., Ltd.), $Ga_2O_3$ (99.9%, Wako Pure Chemical Corp.) and S (High Purity Chemical Laboratory Co., Ltd.) were combined and ground in a glove box under the $N_2$ atmosphere.

### S 1.2 Cocatalyst loading

Impregnation with Rh was carried out by dispersing the particulate photocatalyst in an aqueous

solution containing a specific amount of $RhCl_3 \cdot 3H_2O$. 0.4 wt% Rh was loaded onto 0.2 g photocatalyst using 1~2 mL of an aqueous $RhCl_3 \cdot 3H_2O$ solution. The obtaining slurry was stirred manually with a glass rod and then dried on a water bath. The impregnated material was subsequently heated to 573 K at a rate of 10 K $min^{-1}$ and then held at that temperature for 1 h under a combined flow of $H_2$ at a rate of 20 mL $min^{-1}$ and $N_2$ at a rate of 200 mL $min^{-1}$. The resulting Rh-loaded photocatalyst was subsequently applied to photocatalytic $H_2$ evolution.

S 1.3 Characterization

X-ray diffraction (XRD) patterns were acquired using a Rigaku Miniflex 300 powder diffractometer with Cu Kα radiation. Ultraviolet-visible-near infrared diffuse reflectance spectroscopy (DRS) was performed with a JASCO V-670 spectrometer equipped with an integrating sphere. A Spectralon standard was used as the reference for baseline correction and the reflectance data were converted into the Kubelka-Munk function. X-ray photoelectron spectroscopy (XPS) was carried out using a PHI Quantera II spectrometer, employing Al Kα radiation and using the C 1s line (at 284.6 eV) for calibration. Scanning electron microscopy (SEM) images were acquired with a Phenom Pharos instrument (Thermo Fisher Scientific). Transient absorption spectroscopy (TAS) was carried out under $N_2$ at a pressure of 20 Torr and at room temperature with excitation by 470 nm laser pulses (duration: 6 ns, fluence: 1 mJ/pulse, repetition rate: 1 Hz).

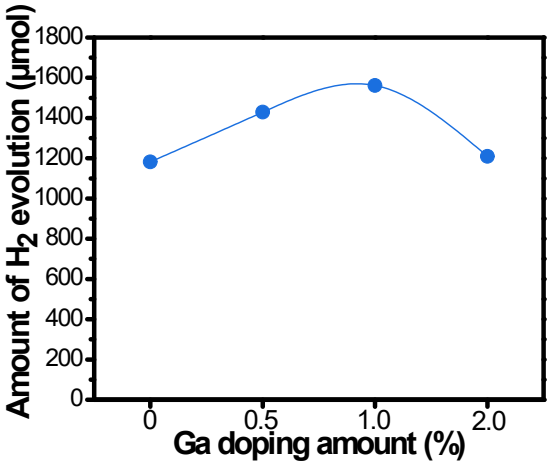


Figure S1. Photocatalytic $H_2$ evolution activity over LTCA as a function of the Ga doping amount. Reaction conditions: photocatalyst amount: 0.2 g; cocatalyst: Rh (0.4 wt%) loaded by impregnation; medium: 100 mL aqueous solution containing 50 mM $Na_2S$ and 50 mM $Na_2SO_3$; background pressure: 6.6 kPa; 300 W Xe lamp; $\lambda > 420$ nm.

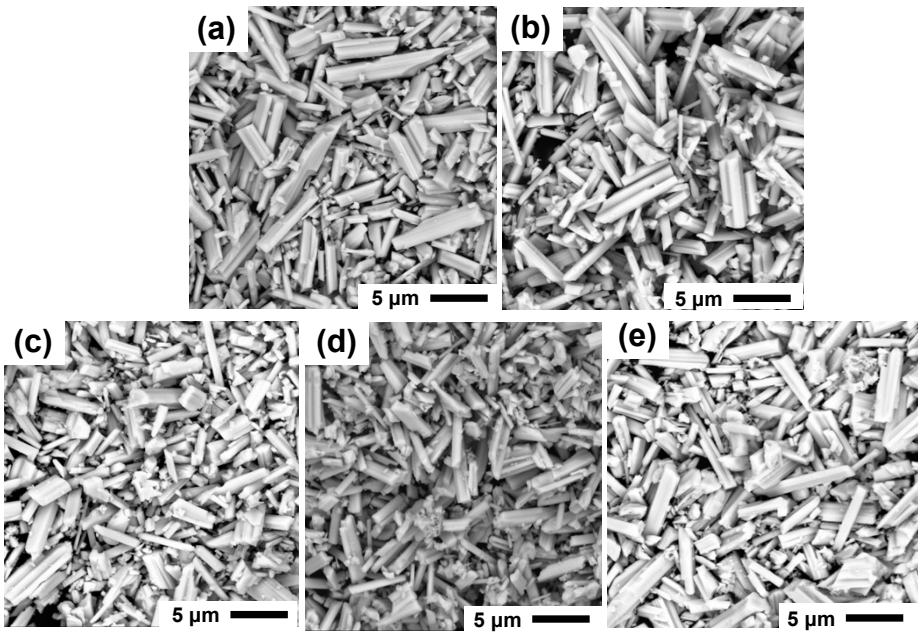


Figure S2. SEM images of (a) LTCA, (b) Ga 1%-LTCA, (c) Ga 1%, Al 0.5%-LTCA, (d) Ga 1%, Al 1%-LTCA and (e) Ga 1%, Al 2%-LTCA particles.

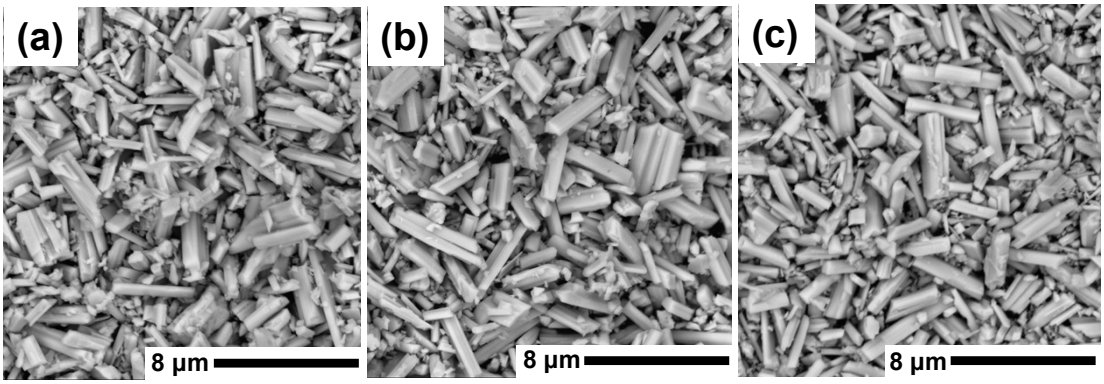


Figure S3. SEM images of Ga 1%, Al 0.5%-LTCA samples after heating for (a) 48, (b) 72 and (c) 96 h under the targeting heating temperature of 1323 K.

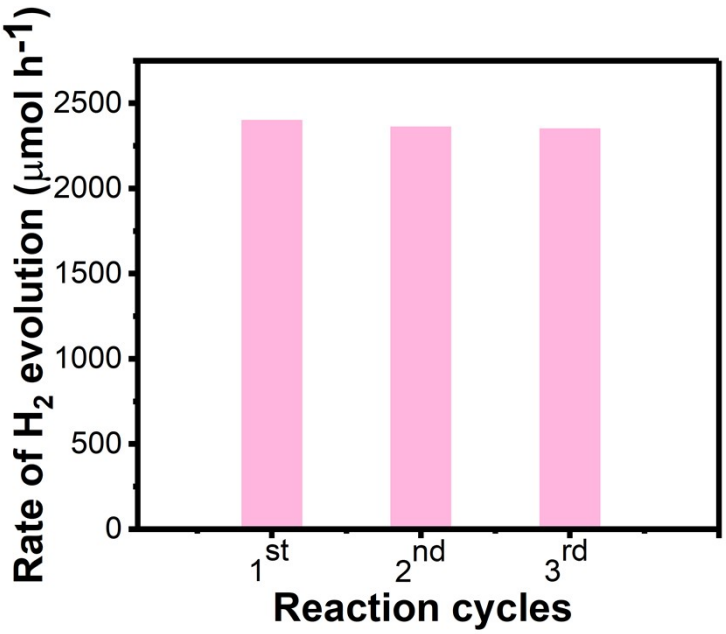


Figure S4. (a) Stability of Ga 1%, Al 0.5%-LTCA samples in the concentration of the reaction solution of 250 mM $Na_2S$-$Na_2SO_3$. Reaction conditions: 0.2 g photocatalyst; cocatalyst: Rh (0.4 wt%) loaded by impregnation method; background pressure, 6.6 KPa; 300 W Xe lamp; $\lambda > 420$ nm.

**Text S2** As shown in Figure S5(a), the undoped LTCA, Ga 1% doped LTCA, Al 0.5% doped LTCA and Ga 1% Al 0.5% co-doped LTCA all generated similar XRD patterns. Each of these materials

also produced a very similar DRS spectrum (Figures S5(b)), likely because the extent of doping with $Ga^{3+}$ and $Al^{3+}$ was minimal. Among these samples, the specimen doped with both Ga and Al provided the highest photocatalytic hydrogen evolution rate. The hydrogen evolution rate decreased in the order of Ga, Al-LTCA > Ga-LTCA > Al-LTCA > LTCA (Figure S5(c)). These materials also had a consistent particle morphology (Figure S6).

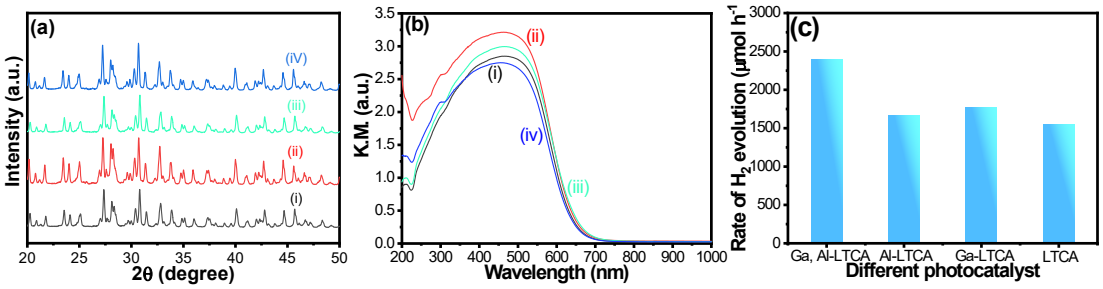


Figure S5. (a) XRD patterns, (b) DRS data and (c) $H_2$ evolution rates for (i) LTCA, (ii) Ga 1%-LTCA, (iii) Al 0.5%-LTCA and (iv) Ga 1%, Al 0.5%-LTCA. The data in (c) were obtained using the reaction conditions: photocatalyst amount, 0.2 g; cocatalyst, Rh (0.4 wt%) loaded by impregnation; medium, 100 mL of an aqueous solution containing 250 mM $Na_2S$ and 250 mM $Na_2SO_3$; background pressure, 6.6 KPa; 300 W Xe lamp; $\lambda > 420$ nm.

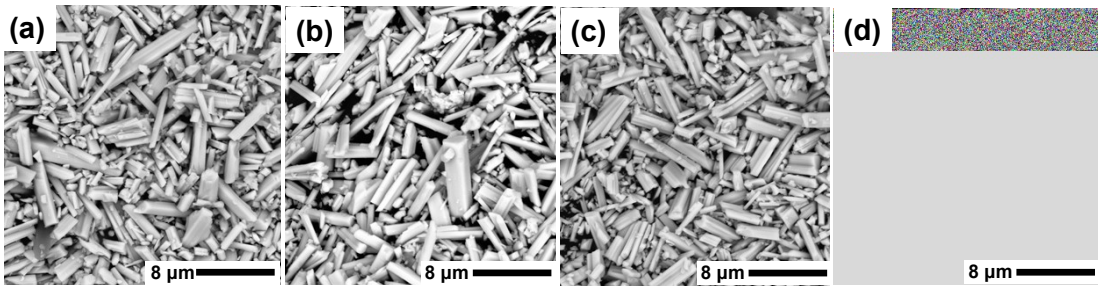


Figure S6. SEM images of (a) LTCA, (b) Ga 1%-LTCA, (c) Al 0.5%-LTCA and (d) Ga 1%, Al 0.5%-LTCA particles.

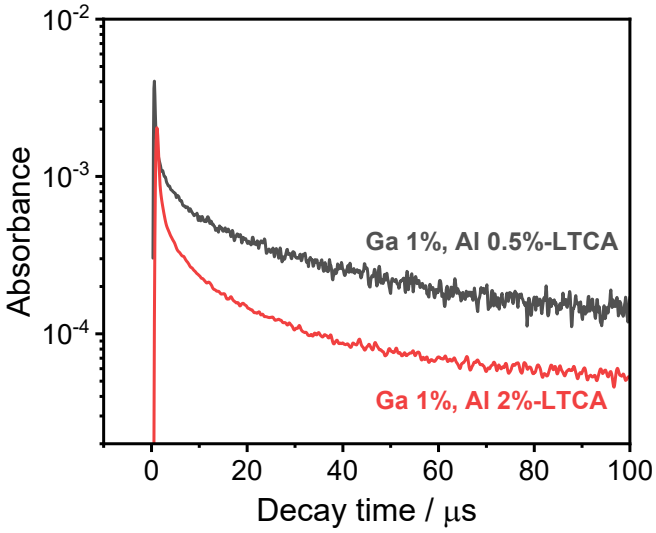


Figure S7. Transient decay profiles of electrons probed at 2000 nm for Ga 1%, Al 0.5%-LTCA and Ga 1%, Al 2%-LTCA excited by 470 nm laser pulses (duration: 6 ns, fluence: 1 mJ pulse$^{-1}$, repetition rate: 1 Hz) under $N_2$ at 20 Torr and at room temperature.