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# Site-selective photodeposition of Pt on a particulate Sc-$La_5Ti_2CuS_5O_7$ photocathode: evidence for one-dimensional charge transfer

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**Contents:**

**Experimental details:**

## 1. Preparation of Sc-doped $La_5Ti_2CuS_5O_7$ (Sc-LTC) powder[1,2]

Sc-LTC powder was prepared by a solid-state reaction. $La_2O_3$ (99.99%, Kanto Chemical), $La_2S_3$ (99.9%, Kojundo Chemical), $TiO_2$ (rutile, 99.0%, Kanto Chemical), $Sc_2O_3$ (99.9%, Kojundo Chemical) and $Cu_2S$ (99%, Kojundo Chemical) in a molar ratio of 2 : 3 : 3.96 : 0.02 : 1 were mixed and ground in a glove box filled with $N_2$. 25 mol% sulfur powder with respect to Sc:LTC was added into the precursor mix to obtain a sulfur-rich atmosphere. The total amount of the precursors was typically 1.5-2.0 g. The mixture was sealed in an evacuated quartz tube ($\phi$8 mm × L 80 mm) and calcined at 1273 K for 48 h. After heating, the sintered samples were ground into powder. The LTC obtained was a highly crystallized, rod-shaped material. The diameters of the LTC rods ranged from 0.7 to 1.4 μm, and their lengths varied from 2 to 6 μm.

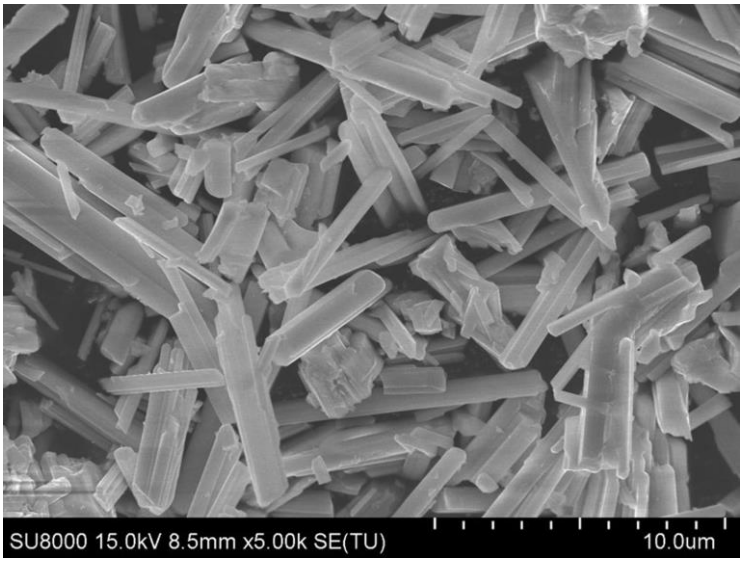


**Figure S1.** SEM image of Sc-LTC powder.

## 2. Fabrication of Sc-LTC/Au photoelectrodes by the particle transfer (PT) method[3]

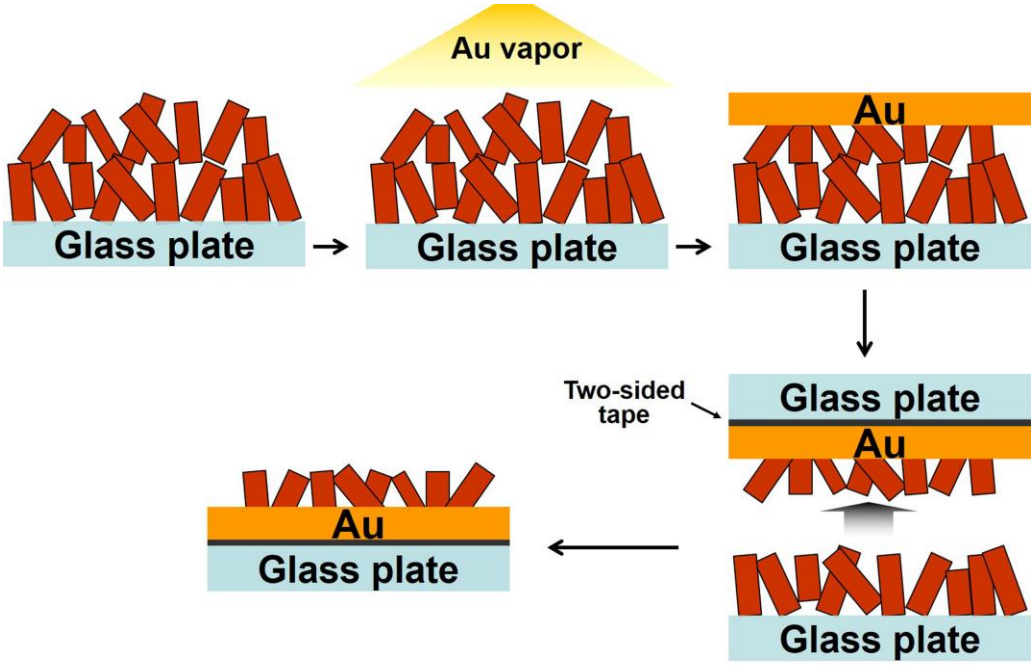


**Figure S2.** Fabrication of LTC/Au electrodes by PT method.

The fabrication process of Sc-LTC/Au photocathodes by the PT method is illustrated in Fig. S2. First, the LTC powder was densely dispersed on a glass plate. Then, a 2.5-μm-thick layer of Au metal was deposited on the top of the LTC powder layer by thermal vapor deposition (TVD). In this process, the top layer of Sc-LTC particles was embedded in the Au film. This ensured an intimate contact between the semiconductor and the metal substrate. The Au film was bonded to a second glass plate by double-sided tape, and then peeled off from the primary glass plate. The physically adsorbed Sc-LTC particles were removed by ultrasonication in water. Finally, the photoelectrode was obtained with a stacked structure of Sc-LTC/Au/tape/glass plate.

## 3. Loading of Pt on Sc-LTC/Au by sputtering[2]

Pt was loaded on Sc-LTC/Au by radio-frequency (RF) magnetron sputtering using high-purity Ar gas as a plasma source. The pressure inside the vacuum chamber was set at $3\times10^{-3}$ Pa during sputtering. Pt with a nominal thickness of approximately 1 nm was loaded on LTC/Au by continuous sputtering for 5 min.

## 4. Loading of Pt on Sc-LTC/Au by photoelectrochemical (PEC) reduction

Pt was loaded on Sc-LTC/Au by PEC reduction using a typical three-electrode system. A Pt wire and Ag/AgCl were used as counter and reference electrodes, respectively. The electrolyte solution used was $H_2O$ (100 mL) containing $Na_2SO_4$ (0.1 M), $K_2C_2O_4$ (0.1 M), and $H_2PtCl_6$ ($3.5\times10^{-6}$ M for PEC measurements and $10\times10^{-6}$ M for SEM and EDX measurements). The pH of the electrolyte solution was adjusted to 10 by an aqueous NaOH solution. Light irradiation was performed using a solar light simulator (AM 1.5 G). The irradiated area of the Sc-LTC/Au electrode was approximately 0.4 $cm^2$. The Pt deposition potential was set to -0.69 V vs. Ag/AgCl. During the reaction, the electrolyte solution was vigorously stirred under flowing Ar. A typical time-current curve for PEC loading of Pt on Sc-LTC/Au is shown in Fig. S3. The reaction was stopped when the photocurrent leveled off. The prepared Pt/Sc-LTC/Ti electrode was washed with copious amounts of deionized water prior to use.

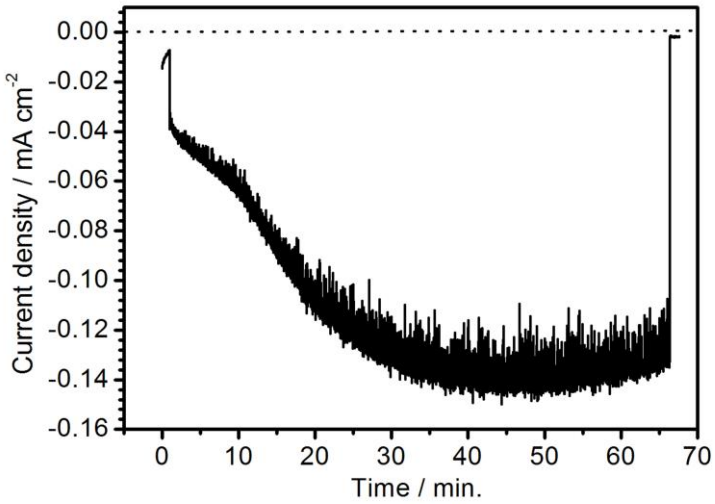


**Figure S3.** Time-current curve for PEC loading of Pt on Sc-LTC/Au photocathode.

The standard redox potentials of some Pt species are listed below:

$PtCl_6^{2-} + 2e^- \rightleftharpoons PtCl_4^{2-} + 2Cl^-$ $E^\circ = 0.68$ V

$PtCl_4^{2-} + 2e^- \rightleftharpoons Pt(s) + 4Cl^-$ $E^\circ = 0.755$ V

$Pt(OH)_2 + 2e^- \rightleftharpoons Pt(s) + 2OH^-$ $E^\circ = 0.14$ V

$Pt^{2+} + 2e^- \rightleftharpoons Pt(s)$ $E^\circ = 1.18$ V

## 5. PEC measurements of Pt/Sc-LTC/Au photocathodes

Current-potential curves of Pt/Sc-LTC/Au were measured in the above PEC system by using a Pt wire and Ag/AgCl as counter and reference electrodes, respectively. The cell was filled with an aqueous solution of 0.1 M $Na_2SO_4$ (pH adjusted to 10 by NaOH addition). A solar light simulator (AM 1.5 G) was used as the light source.

## References


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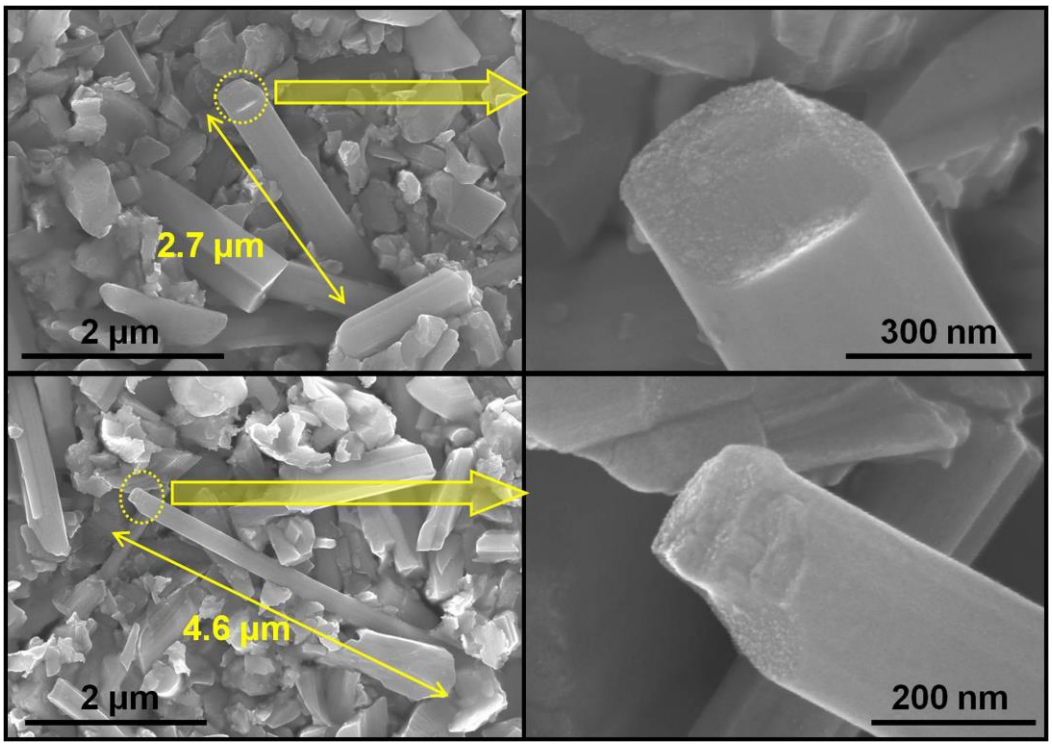


**Figure S4.** SEM images of Pt/Sc-LTC/Au electrodes. The Pt is deposited in a solution containing $Na_2SO_4$ (0.1 M), $K_2C_2O_4$ (0.1 M), and $H_2PtCl_6$ ($10\times10^{-6}$ M).

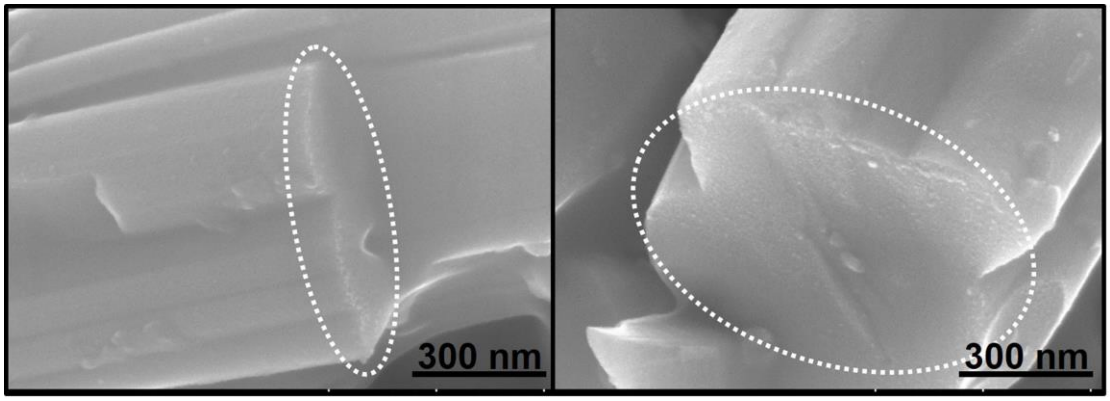


**Figure S5.** SEM images of Pt/Sc-LTC/Au electrodes. The Pt was deposited in a solution containing $Na_2SO_4$ (0.1 M) and $H_2PtCl_6$ ($10\times10^{-6}$ M).

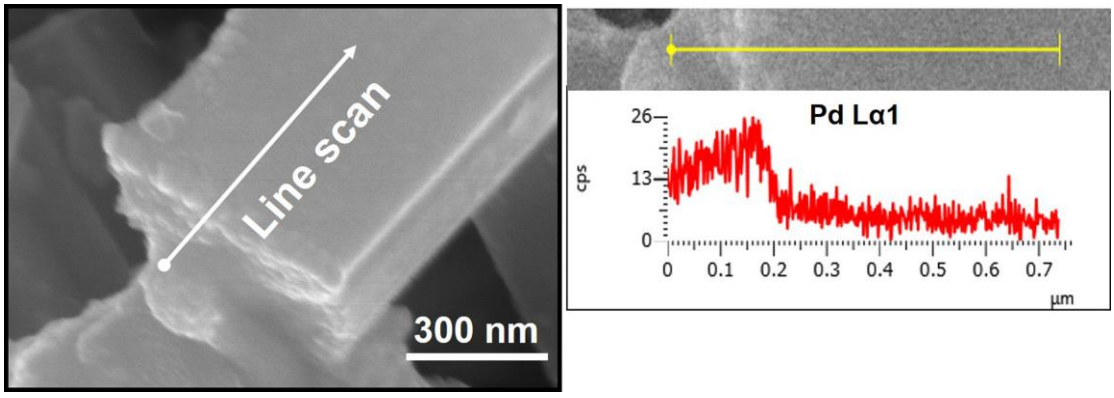


**Figure S6.** SEM and EDX analysis of Pd/Sc-LTC/Au electrodes. The Pd was deposited in a solution containing $Na_2SO_4$ (0.1 M), $K_2C_2O_4$ (0.1 M), and $(NH_4)_2PdCl_4$ ($15\times10^{-6}$ M).

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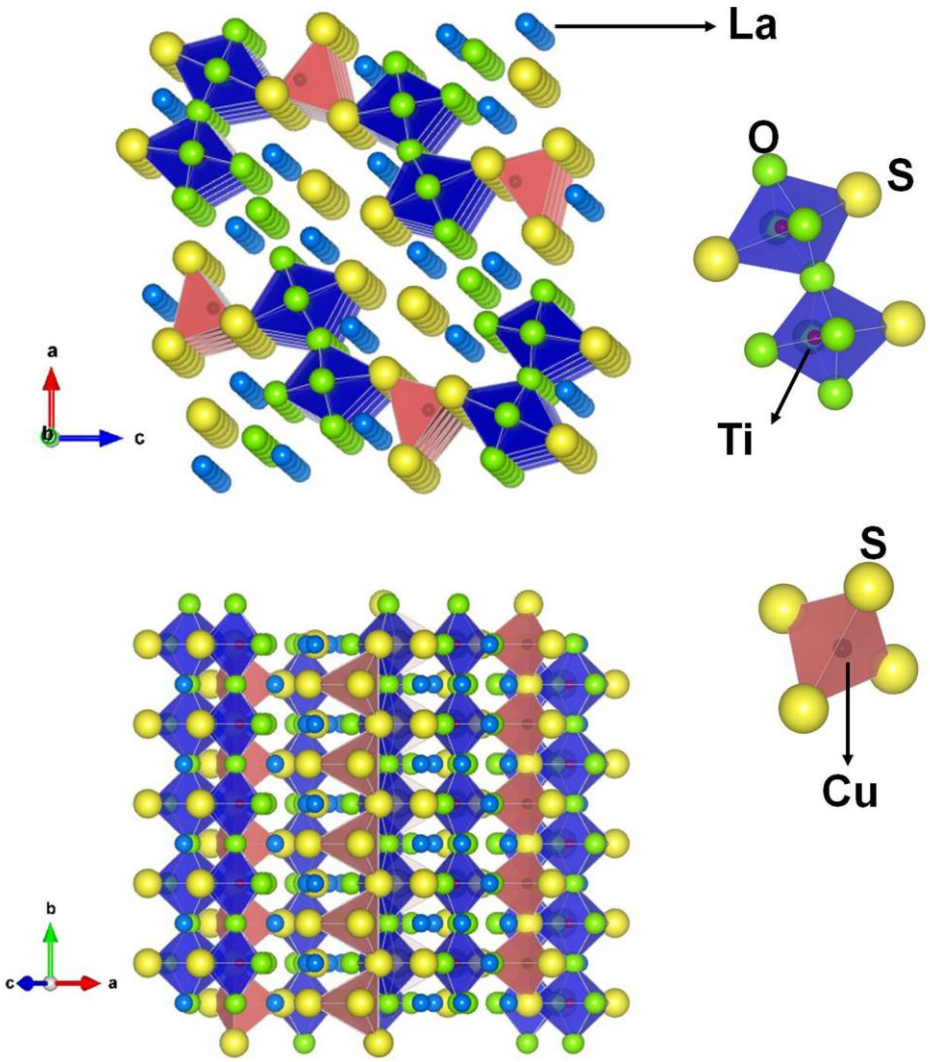


**Figure S7.** Crystal structure of $La_5Ti_2CuS_5O_7$ viewed along b and c axes (depicted using Vesta[4]).