Site-selective photodeposition of Pt on a particulate Sc-La₅Ti₂CuS₅O₇ photocathode: evidence for one-dimensional charge transfer

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Experimental details:

1. Preparation of Sc-doped La$_5$Ti$_2$CuS$_5$O$_7$ (Sc-LTC) powder$^{1,2}$

Sc-LTC powder was prepared by a solid-state reaction. La$_2$O$_3$ (99.99%, Kanto Chemical), La$_2$S$_3$ (99.9%, Kojundo Chemical), TiO$_2$ (rutile, 99.0%, Kanto Chemical), Sc$_2$O$_3$ (99.9%, Kojundo Chemical) and Cu$_2$S (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 $\times$ 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.](image-url)
2. Fabrication of Sc-LTC/Au photoelectrodes by the particle transfer (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

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 3×10⁻³ 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 H₂O (100 mL) containing Na₂SO₄ (0.1 M), K₂C₂O₄ (0.1 M), and H₂PtCl₆ (3.5×10⁻⁶ M for PEC measurements and 10×10⁻⁶ 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 cm². 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:

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\begin{align*}
\text{PtCl}_6^{2-} + 2e^- & \rightleftharpoons \text{PtCl}_4^{2-} + 2\text{Cl}^- \quad E^\circ = 0.68 \text{ V} \\
\text{PtCl}_4^{2-} + 2e^- & \rightleftharpoons \text{Pt(s)} + 4\text{Cl}^- \quad E^\circ = 0.755 \text{ V} \\
\text{Pt(OH)}_2 + 2e^- & \rightleftharpoons \text{Pt(s)} + 2\text{OH}^- \quad E^\circ = 0.14 \text{ V} \\
\text{Pt}^{2+} + 2e^- & \rightleftharpoons \text{Pt(s)} \quad E^\circ = 1.18 \text{ V}
\end{align*}
\]

**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$_2$SO$_4$ (pH adjusted to 10 by NaOH addition). A solar light simulator (AM 1.5 G) was used as the light source.
References


Figure S4. SEM images of Pt/Sc-LTC/Au electrodes. The Pt is deposited in a solution containing Na$_2$SO$_4$ (0.1 M), K$_2$C$_2$O$_4$ (0.1 M), and H$_2$PtCl$_6$ (10$\times$10$^{-6}$ M).
Figure S5. SEM images of Pt/Sc-LTC/Au electrodes. The Pt was deposited in a solution containing Na$_2$SO$_4$ (0.1 M) and H$_2$PtCl$_6$ (10×10$^{-6}$ M).
Figure S6. SEM and EDX analysis of Pd/Sc-LTC/Au electrodes. The Pd was deposited in a solution containing Na$_2$SO$_4$ (0.1 M), K$_2$C$_2$O$_4$ (0.1 M), and (NH$_4$)$_2$PdCl$_4$ (15×10$^{-6}$ M).
Figure S7. Crystal structure of La₅Ti₂CuS₅O₇ viewed along b and c axes (depicted using Vesta⁴).