Photoanodic and photocathodic behaviours of La₅Ti₂CuS₅O₇ electrodes in the

water splitting reaction

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Experimental Details:

1. Preparation of La₅Ti₂CuS₅O₇ (LTC) powder^{1,2}

LTC powder was prepared by a solid state reaction. A mixture of La₂O₃ (99.99%, Kanto Chemical), La₂S₃ (99.9%, Kojundo Chemical), TiO₂ (rutile, 99.0%, Kanto Chemical) and Cu₂S (99%, Kojundo Chemical) were mixed at a molar ratio of 2:3:4:1 in a glove box filled with N₂. Sulphur powder (99.99%, Kojundo Chemical), 25 mol% with respect to LTC, was added into the precursor mixture to provide a sulphur-rich atmosphere during calcination in an evacuated sealed tube. The precursor mixture (1.5-2.0 g) was sealed in an evacuated quartz tube (ϕ 8 mm × *L* 80 mm) and calcined at 1273 K for 48 h. After calcination, the sintered samples were pulverized. The LTC produced was characterized by X-ray diffraction (XRD; RINT-Ultima III, Rigaku; Cu K) and scanning electron microscopy (SEM; S-4700, Hitachi).

2. Fabrication of LTC/metal photoelectrodes by the particle transfer (PT) method³

The process of fabricating LTC/metal photoelectrodes by the PT method is illustrated in Scheme S1. First, the LTC powder was spread densely on a glass plate. Then, a roughly 2.5 µm-thick layer of metal (Au or Ti) was deposited on the LTC powder by vacuum evaporation (for Au) or radio-frequency magnetron sputtering (for Ti). During this process, the top layer of LTC particles was embedded into the metal film, and thus, an intimate contact was formed between the semiconductor particles and the metal layer. The metal films were bonded to a second glass plate by doubleface tape and then peeled off of the primary glass plate. Thus, photoelectrodes of LTC/metal/tape/glass plate were obtained.

3. Loading of Pt on LTC/Au by sputtering

Pt was loaded as a H_2 evolution catalyst on an LTC/Au photoelectrode by a laboratory-built radio-frequency magnetron sputtering system using high-purity Ar gas as a plasma source. The pressure inside the vacuum chamber was set to 3×10^{-3} Pa during the sputtering. Pt with a nominal thickness of 1 nm was loaded on LTC/Au at room temperature in 5 min.

4. Loading of cobalt phosphate (CoPi) on LTC/Ti by electrodeposition⁴

CoPi was loaded as an O₂ evolution catalyst on the surface of an LTC/Ti photoelectrode by electrodeposition (ED). An aqueous solution of potassium phosphate (0.1 M, buffered at pH 7) was used as ED solution. The ED conditions were optimized: 0.4 V vs. Ag/AgCl for 15 min. After ED, the CoPi/LTC/Ti was washed with copious amounts of distilled water before use.

5. PEC measurements of LTC/metal photoelectrodes

Current-potential curves of LTC/metal photoelectrodes were measured in a typical three-electrode system. The cell was filled with an aqueous solution of 0.1 M Na₂SO₄, and the pH value of the electrolyte was adjusted to 12 by NaOH. The counter and reference electrodes used for PEC measurements were Pt wire and an Ag/AgCl electrode, respectively. Light with wavelengths between 420 and 800 nm was obtained using a 300 W xenon (Xe) lamp equipped with a mirror module and a cutoff filter.

6. Detection of gaseous products on LTC/metal photoelectrodes

The evolved H_2 and O_2 gases were detected in an Ar-filled two-electrode system using the same electrolyte solution and light source as above. For the half reactions, Pt/LTC/Au or CoPi/LTC/Ti was used as a working electrode, and Pt wire was used as a counter electrode. In the case of overall PEC water splitting, CoPi/LTC/Ti and Pt/LTC/Au were connected in series. The amounts of evolved H_2 and O_2 were measured with an on-line micro gas chromatograph (Agilent 3000A).

7. Determination of the valence band edge of LTC by photoelectron spectroscopy

The energy level of the top of the valence band of the LTC semiconductor was determined by photoelectron spectroscopy under atmospheric pressure (PESA, Riken Keiki AC-3). An LTC/Au sample was irradiated by UV light (8 nW) under flowing N_2 , and the signal was recorded in the range from 4.0 to 7.0 eV. The spot size of the UV light was 2.5×5.0 mm. A gold wafer was used as reference. As shown in Figure S3, the top of the valence band of LTC was found to be 5.7 eV.

8. Transient absorption spectroscopy (TAS)^{5,6}

For the femtosecond time-resolved diffuse reflectance (fs-TRDR) measurements, a fundamental beam from a femtosecond Ti:sapphire laser with a regenerative amplifier (Hurricane, Spectra Physics, 800 nm, 130 fs, 1 mJ/pulse, 1 kHz) coupled with an optical parametric amplifier (OPA) (TOPAS, Quantronix) was used to generate pump pulses at 535 nm. The LTC powder sample was transferred into a 0.5 mm detachable quartz cuvette. The pump beam diameter on the sample surface was about 0.5 mm, as observed with a CCD camera. The probe beam was a white light continuum generated by focusing a part of the fundamental from the Ti-sapphire laser into a sapphire plate (450-1200 nm). An amplified Si photodetector was used, and the diffuse reflected probe beam was detected after passing through a grating monochromator (Acton Research, SpectraPro-150). Measurements were performed in air at room temperature. The transient absorption intensity estimates at the probed wavelength were expressed as percentage absorption (%A). %A = $100\% \times (1-R/R_0)$, where R and R_0 are the intensities of the diffuse reflected light with and without excitation, respectively. For simplicity, however, this paper presents data normalized at zero delay time. The transient absorption monitored at 900 nm was considered in this work because %A became the strongest at 900 nm and decayed in similar time scales over the measured spectrum and temporal ranges (650–1000 nm and 1 ps–2 ns).

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Parameter of LTC	Value
Thickness	2 μm
Dielectric constant	10
Electron affinity	3.8 eV
Band gap	1.9 eV
Density of state - conduction band	$10^{19}{\rm cm}^{-3}$
Density of state - valence band	$10^{19}{\rm cm}^{-3}$
Electron mobility	1000 cm ² V ⁻¹ s ⁻¹
Hole mobility	500 cm ² V ⁻¹ s ⁻¹
Acceptor concentration for p-type	$10^{15} \mathrm{cm}^{-3}$
Acceptor & donor concentration for intrinsic-type	0 cm ⁻³
Donor concentration for n-type	$10^{15} \mathrm{cm}^{-3}$

Table S1. LTC parameters used in the calculation of the band diagram.

* The Fermi levels of the LTC are evaluated from the assumed dopant concentrations.



Figure S1. Power spectra of (a) the Xe lamp and (b) the standard AM1.5G irradiation.

The power spectrum of the Xe lamp was measured through a neutral density filter (transmittance = 12%).



Figure S2. X-ray diffraction pattern of La₅Ti₂CuS₅O₇ powder.



Figure S3. Scanning electron micrograph of La₅Ti₂CuS₅O₇ powder.



Figure S4. Photoelectron spectrum of La₅Ti₂CuS₅O₇ under atmospheric pressure.