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Supporting Information for

Improving the photoelectrochemical activity of $La_5Ti_2CuS_5O_7$ for hydrogen evolution by particle transfer and doping

List of the authors

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Experimental details

$La_5Ti_2CuS_5O_7$ was prepared by solid-state reactions.[S1] First, La_2O_3 (99.99%, Kanto Chemical Co., Inc.), La_2S_3 (99.9%, Kojundo Chemical Laboratory Co., Ltd.), TiO_2 (99.99%, Rare Metallic Co., Ltd.) and Cu_2S (99%, Kojundo Chemical Laboratory Co., Ltd.) were mixed at a molar ratio of La_2O_3:La_2S_3:TiO_2:Cu_2S = 2:3:4:1 in a N_2 circulated glove box. For substitution of Ta, Nb, Sc and Ga at the Ti site of $La_5Ti_2CuS_5O_7$, the amount of TiO_2 was decreased and the corresponding amounts of Ta_2O_5 (99.9%, Wako Pure Chemical Industries, Ltd.), Nb_2O_5 (Optical grade, CBMM), Sc_2O_3 (99.95%, Kanto Chemical Co., Inc.) and Ga_2O_3 (99.9%, Kojundo Chemical Laboratory Co., Ltd.) were added. For substitution of Ca at the La site, the amount of La_2O_3 was decreased and the corresponding amount of CaO (99.9%, Wako Pure Chemical Industries., Ltd.) was added. The precursor mixture was sealed in evacuated quartz tubes and heated at 1273 K for 48 h. After heating, the samples were ground into powder. During the heating process at high temperature under vacuum, metal sulphide could decompose to produce gaseous sulphur and metal cations could be reduced. To suppress this, the vapour pressure of sulphur inside the quartz tubes was increased by deliberately adding 5% excess sulphur (99.99%, Kojundo Chemical Laboratory Co., Ltd.) into the precursor mixtures. The $La_5Ti_2CuS_5O_7$ samples prepared with excess sulphur are denoted as $La_5Ti_2CuS_5O_7$(S). The samples were characterized by X-ray diffraction (XRD, RIGAKU, RINT Ultima III), UV-Visible diffuse reflectance spectroscopy (UV-vis DRS, JASCO, V-560), and field-emission scanning electron microscopy (FE-SEM, Hitachi, S-4700). Cu-K edge X-ray absorption near edge structures (XANES) were measured at the BL9C beamline of the Photon Factory (High Energy Accelerator Research Organization, Tsukuba, Japan) using a ring energy of 2.5 GeV and stored current of 400 mA (Proposal No. 2012G650).

Photocatalytic reactions were carried out in a Pyrex reaction vessel connected to a glass closed gas circulation system. A solution (200 mL) of Na_2S (0.01 M) and Na_2SO_3 (0.01 M) was used for the H_2 evolution reactions. A solution containing 0.20 g of a photocatalyst was evacuated until the air was removed completely and then irradiated with a 300-W Xe lamp through a cutoff filter (λ > 420 nm). Pt was deposited as a catalyst for H_2 evolution by impregnation of $H_2PtCl_6 \cdot 6\,H_2O$, followed by H_2 reduction at 473 K. The reactant solution was maintained at room temperature by a flow of cooling water during the reaction. The evolved gases were analysed by gas chromatography.

Electrodes of $La_5Ti_2CuS_5O_7$ were made by the particle transfer method.[S2] $La_5Ti_2CuS_5O_7$ powder was dispersed in 2-propanol and deposited on a glass plate. After the 2-propanol dried off, a 2-µm-thick Au layer was deposited on the sample as a contact layer by vacuum evaporation. Then, a carbon tape supported by a glass slide was used to peel off the Au layer and $La_5Ti_2CuS_5O_7$ powder from the original glass plate. Excess particles were removed by sonication. Subsequently, 1-nm-thick Pt was deposited as a catalyst by radio frequency magnetron sputtering. The final structure of the electrodes was Pt/$La_5Ti_2CuS_5O_7$/Au/carbon tape/glass from top to bottom. Scanning electron microscope (SEM) images of 1%Sc doped-$La_5Ti_2CuS_5O_7$(S) electrode is shown in Fig. S9. In some experiments, 1-nm-thick Ni was deposited instead of Pt by vacuum evaporation. An electric wire was connected to the surface of the electrode using indium solder and covered with epoxy resin.

The PEC measurement was carried out in a three-electrode system, using Pt and Ag/AgCl electrodes as counter and reference electrode, respectively. A solution (100 mL) of 0.1 M Na_2SO_4 was used as electrolyte solution. The pH of the solution was adjusted to 10 by NaOH. A 300-W Xe lamp was used as a light source. Photoelectrodes were irradiated through a cutoff filter (λ > 420 nm). The potential of the electrode was controlled by a potentiostat (Hokutodenko, HSV-100). IPCE was measured at 0 V vs. RHE under the illumination of a 300-W Xe lamp equipped with a series of band pass filters.

References

S1 V. Meignen, L. Cario, A. Lafond, Y. Moëlo, C. Guillot-Deudon, A. Meerschaut, *J. Solid State Chem.*, 2004, **177**, 2810.

S2 T. Minegishi, N. Nishimura, J. Kubota, K. Domen, *Chem. Sci.*, 2013, **4**, 1120.

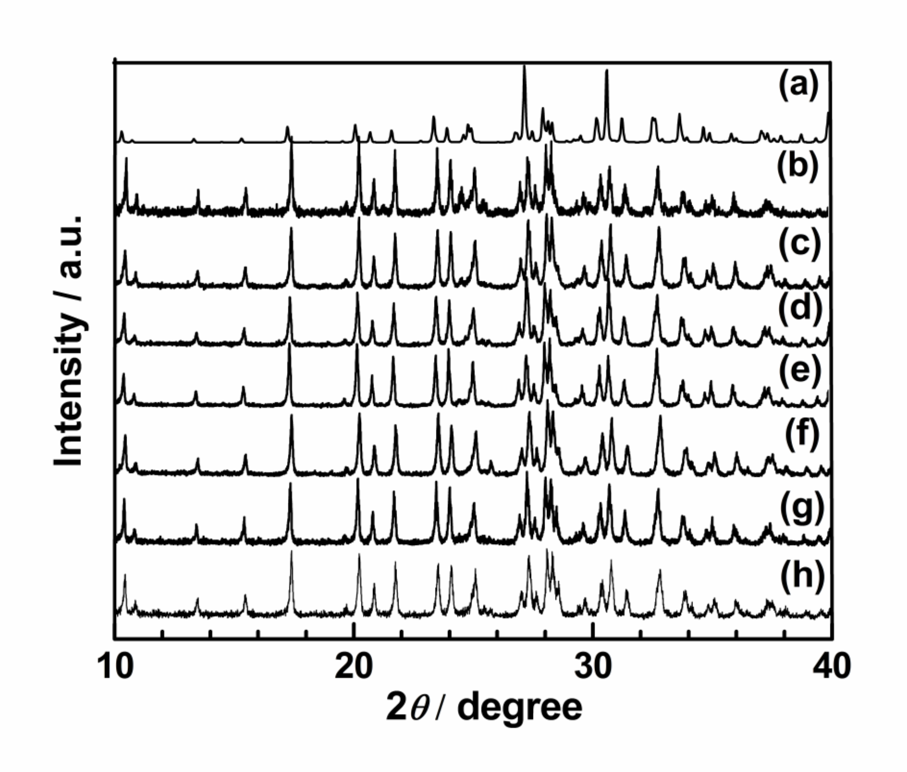

Figure S1. XRD patterns for (a) the reference $La_5Ti_2CuS_5O_7$ (ICSD #99612), (b) $La_5Ti_2CuS_5O_7$, and (c) undoped, (d) 1% Sc-doped, (e) 1% Ga-doped, (f) 1% Ca-doped (g) 1% Ta-doped and (h) 1% Nb-doped $La_5Ti_2CuS_5O_7$(S).

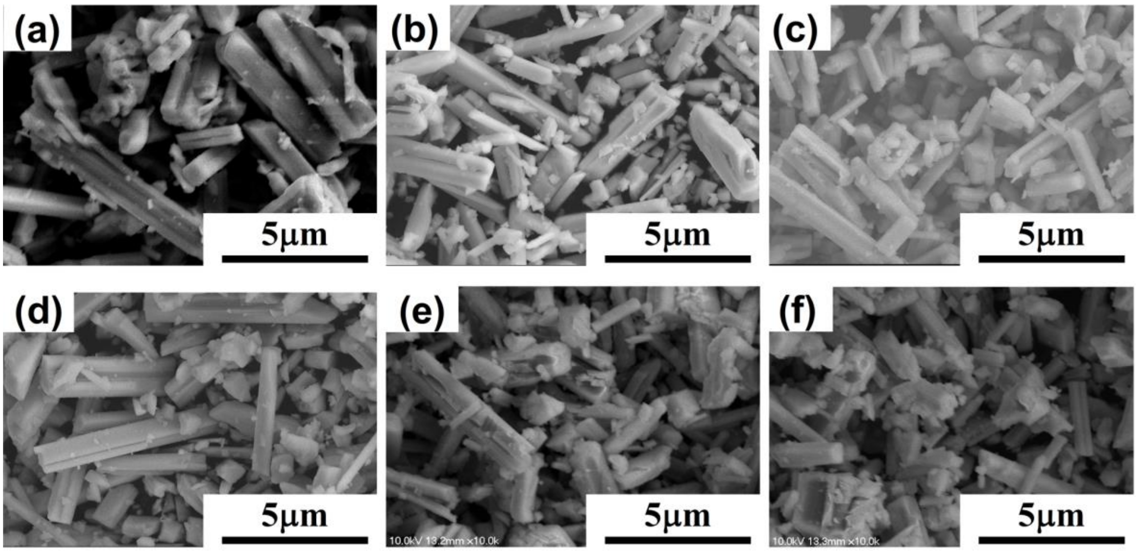

Figure S2. SEM images of (a) $La_5Ti_2CuS_5O_7$, and (b) undoped, (c) 1% Sc-doped, (d) 1% Ga-doped, (e) 1% Ta-doped, and (f) 1% Nb-doped $La_5Ti_2CuS_5O_7$(S).

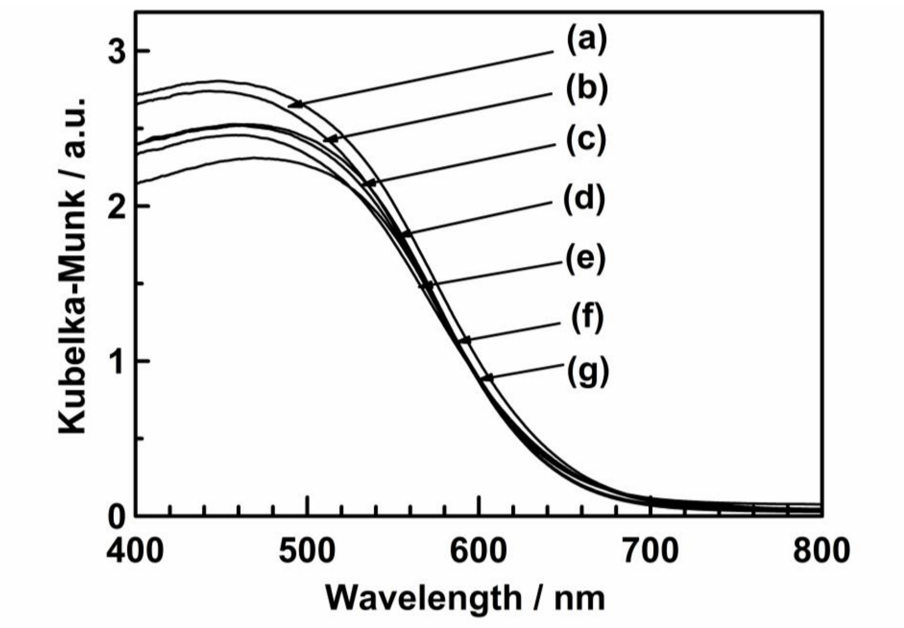

Figure S3. DRS of (a) $La_5Ti_2CuS_5O_7$, and (b) undoped, (c) 1% Sc-doped, (d) 1% Ga-doped, (e) 1% Ca-doped, and (f) 1% Ta-doped, and (g) 1% Nb-doped $La_5Ti_2CuS_5O_7$(S).

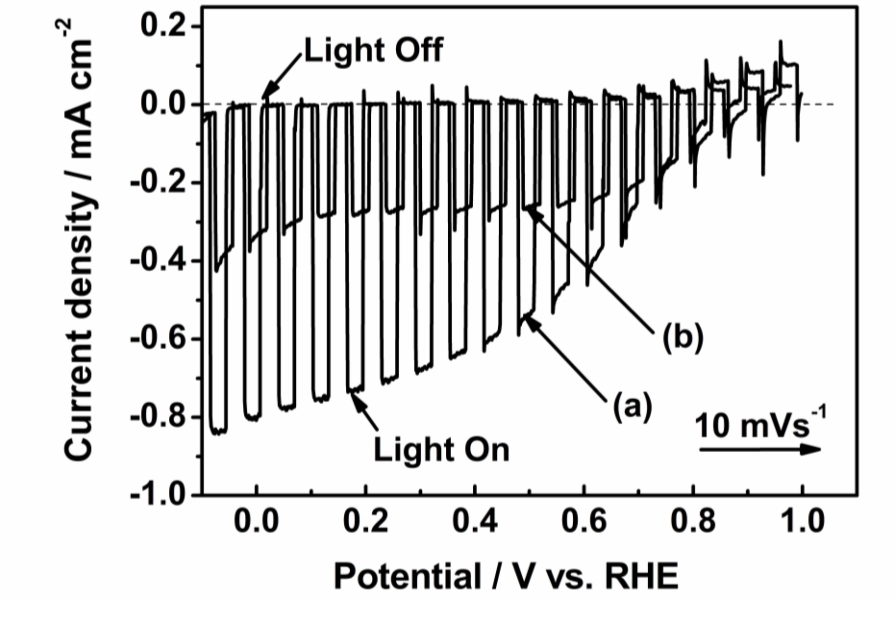

Figure S4. *I*-*E* curves for 1% Sc-doped $La_5Ti_2CuS_5O_7$(S) photocathodes modified with (a) 1-nm0thick Pt and (b) 1-nm-thick Ni. Electrolyte, Na_2SO_4 aq (pH 10); light source, 300-W Xe lamp (λ > 420 nm).

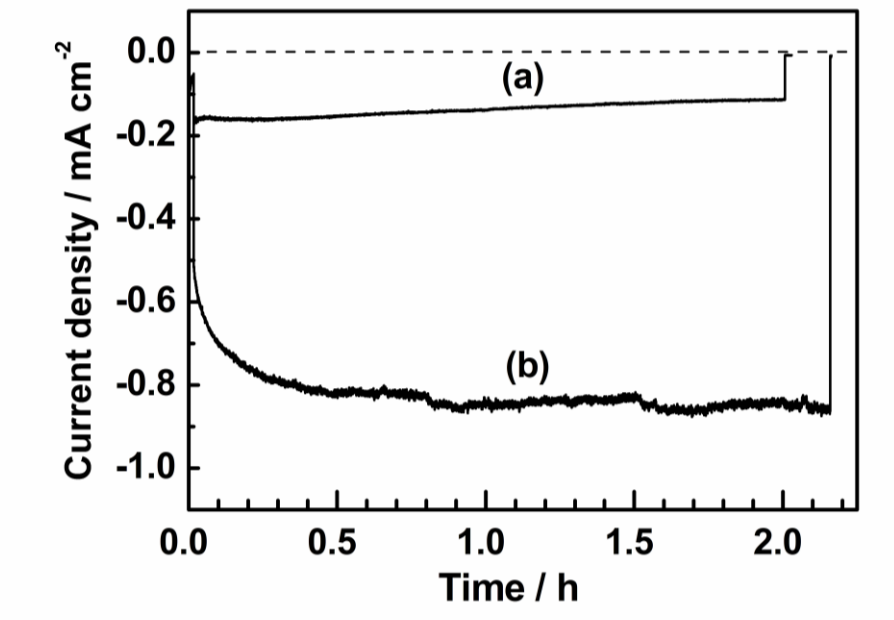

Figure S5. Time course of current density for (a) undoped and (b) 1% Sc-doped $La_5Ti_2CuS_5O_7$(S) photocathodes under irradiation at 0 V vs. RHE. Electrolyte, Na_2SO_4 aq (pH 10); light source, 300-W Xe lamp (λ > 420 nm).

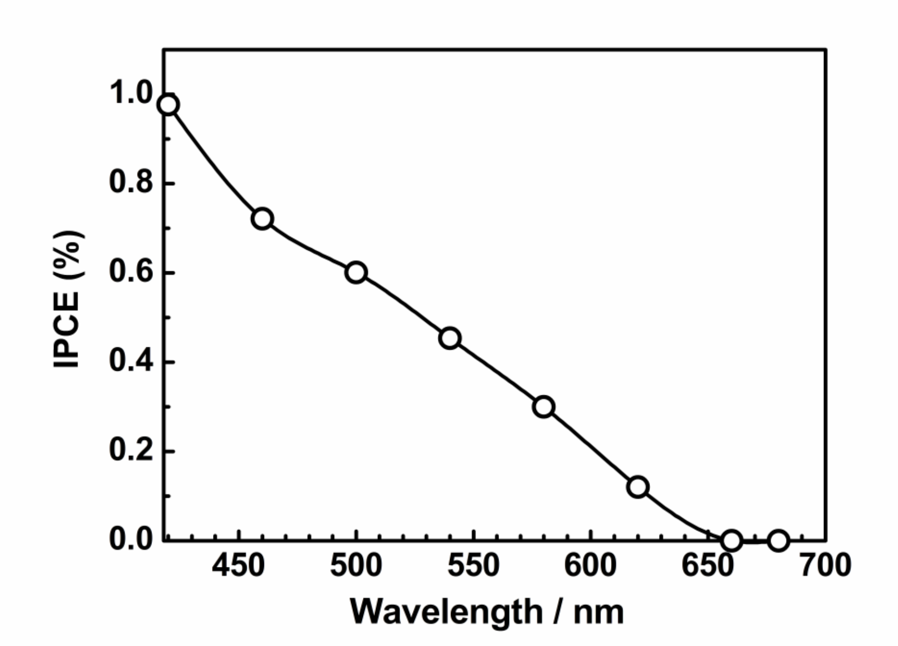

Figure S6. IPCE spectrum of 1% Sc-doped $La_5Ti_2CuS_5O_7$(S). Pt was deposited by sputtering for H_2 evolution. Electrolyte, Na_2SO_4 aq (pH 10); light source, 300-W Xe lamp equipped with various band pass filters.

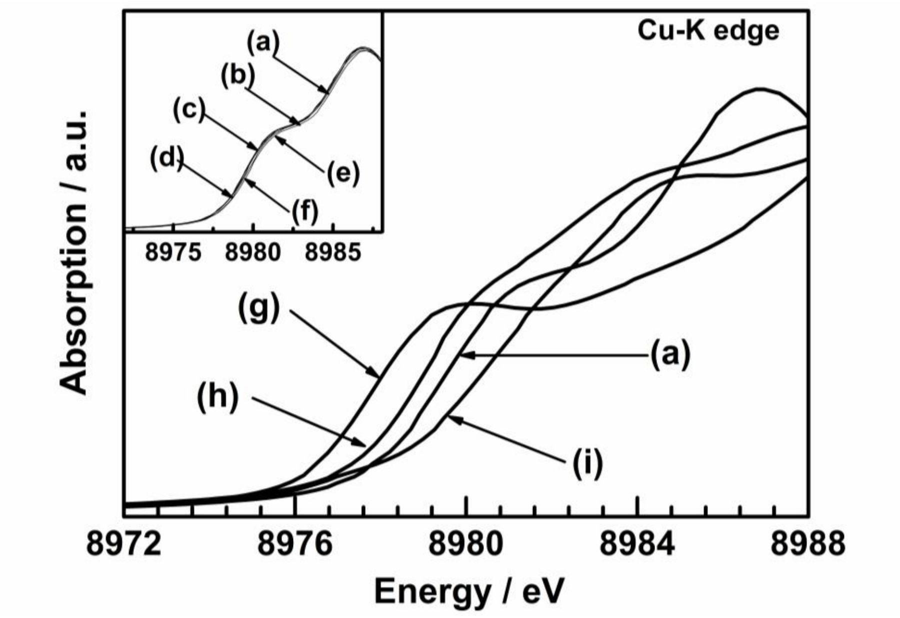

Figure S7. Cu-K edge XANES curves for (a) undoped, (b) 0.1% Sc-doped, (c) 1% Sc-doped, (d) 3%Sc-doped, (e) 5% Sc-doped, (f) 10% Sc-doped $La_5Ti_2CuS_5O_7$(S), (g) Cu, (h) Cu_2S, and (i) CuS.

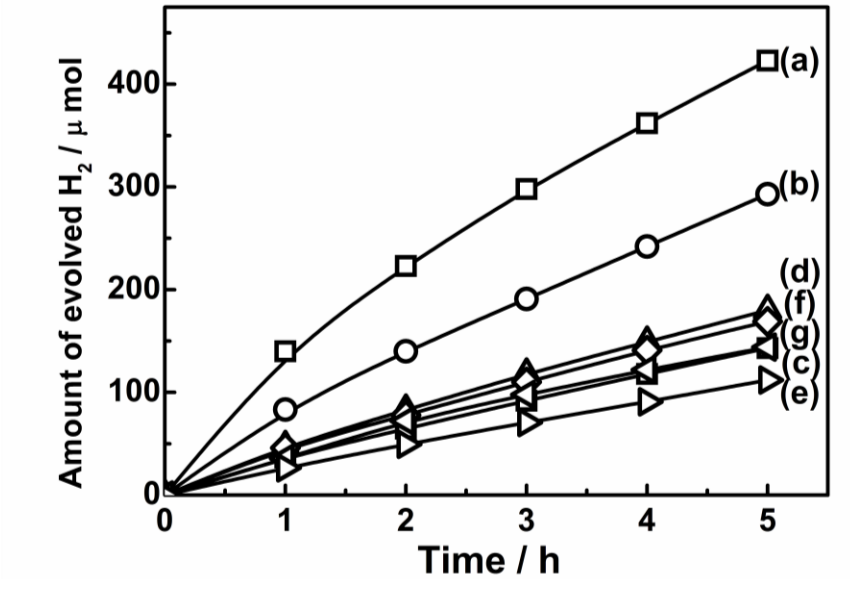

Figure S8. H_2 evolution rates for (a) $La_5Ti_2CuS_5O_7$, and (b) undoped, (c) 1% Sc-doped, (d) 1% Ga-doped, (e) 1% Ca-doped, (f) 1%Ta-doped, and (g) 1% Nb-doped $La_5Ti_2CuS_5O_7$(S). Pt was deposited by impregnation for H_2 evolution. Sacrificial reagent (200 ml), Na_2S aq (0.01 M) and Na_2SO_3 aq (0.01 M); light source, 300-W Xe lamp ($\lambda > 420$ nm).

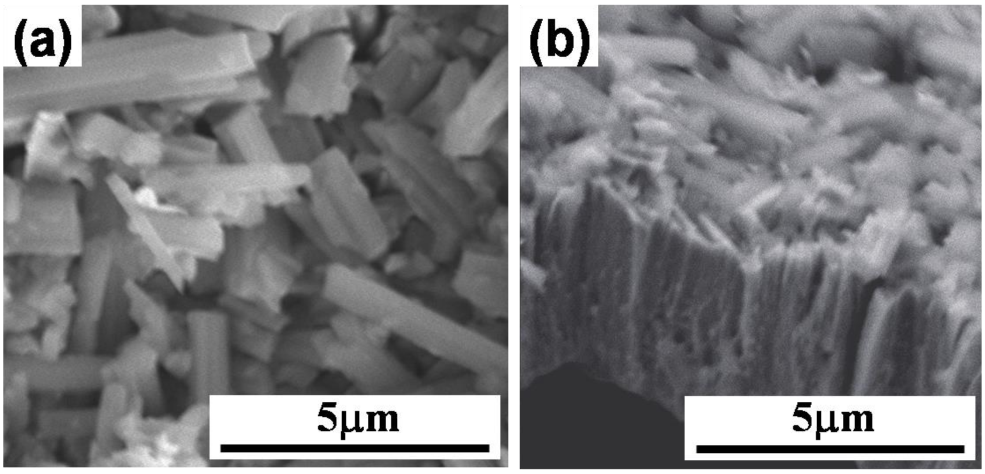

Figure S9. (a) Top-view and (b) cross-sectional SEM images of a 1% Sc doped-$La_5Ti_2CuS_5O_7$ (S) electrode prepared by the PT method.