Supporting Information

Creation of perovskite LaFeO$_3$ network as photoelectrode materials using a salicylate-ligating lanthanum-iron complex precursor

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**Experimental**

**Chemicals**

Methanol (99.9 %), 2-butanol, and triethylamine were used as purchased from Wako. \( \text{La(NO}_3\text{)}_3 \cdot 6\text{H}_2\text{O} \) and \( \text{Fe(NO}_3\text{)}_3 \cdot 9\text{H}_2\text{O} \) were purchased from Wako. Hexylsalicylate was used as purchased from Fluka. \( \text{H}_2\text{O} \) (resistivity: 18.2 MΩcm) obtained from the Milli-Q® integral water purification system was used for the sol-gel synthesis.

**Synthesis of LaFe complex precursor using hexylsalicylate (H-Hesa)**

Trimethylamine (0.74 g, 7.31 mmol) was added to a methanol solution (20 mL) of hexylsalicylate (1.00 g, 4.50 mmol) at ambient temperature. The mixture of \( \text{La(NO}_3\text{)}_3 \cdot 6\text{H}_2\text{O} \) (0.55 g, 1.27 mmol) and \( \text{Fe(NO}_3\text{)}_3 \cdot 9\text{H}_2\text{O} \) (0.51 g, 1.27 mmol) dissolved in methanol (~10 mL) was then added to this solution with stirring at 40 °C for 10–20 min. The solvent was evaporated at ambient temperature to produce a dark reddish–brown slurry, which was used for subsequent sintering at 600, 700 and 800 °C for 2 h. in ambient air to obtain a brown powder.

**Preparation of LaFeO\textsubscript{3} crystals using sol-gel method**

LaFeO\textsubscript{3} crystals were also synthesized for comparison using a reported sol-gel method.\(^1\) \( \text{La(NO}_3\text{)}_3 \cdot 6\text{H}_2\text{O} \) (5.41 g, 12.5 mmol), \( \text{Fe(NO}_3\text{)}_3 \cdot 9\text{H}_2\text{O} \) (5.05 g, 12.5 mmol), and citric acid (4.80 g, 2.50 mmol) were dissolved in water (12.5 mL). After adjusting the pH of the reaction mixture to 6–7, the obtained sample was dried at 80 °C for 30 min. and 130 °C for 60 min. The powder sample was then sintered at 600, 700 and 800 °C for 2 h. in ambient air to obtain a brown powder.
Characterization of LaFe precursor and LaFeO$_3$ crystals

MALDI-TOF mass spectra of the Hesa-derived LaFe complex precursor were obtained using SHIMAZU AXIMA-Resonance mass spectrometer. Thermogravimetry/differential thermal analysis (TG/DTA) measurements were performed using SHIMAZU TG-50 and DTA-50. The sintered LaFeO$_3$ samples were characterized using XRD, scanning electron microscopy (SEM), EDX, and transmission electron microscopy (TEM). These measurements were carried out on Rigaku RINT-Ultima/PC with monochromated Cu Kα radiation, HITACHI S-4800, S-4300, and JEM-2100, respectively. The BET surface areas were evaluated by N$_2$ physisorption at 77K using Micrometrics Tristar 3020.

Preparation of LaFeO$_3$ photoanodes and electrochemical measurement

The LaFeO$_3$ powder (0.05 g) was stirred in 2-butanol (0.4 mL) for 24 h. and the obtained mixture was spread on titanium foil (Nilaco) with a glass bar while placing scotch tapes at the edge of the titanium foil. The substrate was then sintered at 500 °C for 2 h. in ambient air. The three-electrode cell consisting of the LaFeO$_3$/Ti photoanode (1cm$^2$), saturated calomel electrode (SCE), and platinum electrode was adapted in combination with the aqueous Na$_2$SO$_4$ electrolyte solution (pH 7). Current-voltage curves were obtained using a potentiostat (HOKUTO DENKO HZ-5000). A 500 W super high-pressure mercury lamp (Ushio) designed for maximum output in the wavelength area of 436, 405, and 365 nm was irradiated to the photoanode. The measurements were performed under intermittent light irradiation ($\lambda > 420$ nm) using a sharp cut filter (SIGMAKOKI SCF-50S-42L).
The donor density \( N_d \) of LaFeO\(_3\) electrodes was determined by Mott-Schottky analysis using equation (1). \( E, E_{FB}, \) and \( c \) indicate the applied potential, flat band potential and space charge capacitance in the electrode, respectively. \( T, k, e, \varepsilon_0, \) and \( \varepsilon \) are the temperature, Boltzmann constant, elemental charge, vacuum permittivity, and relative permittivity, respectively. With equation (2), the relative permittivity of 220 was used for obtaining the \( N_d. \) The Mott-Schottky plots were obtained using a VersaSTAT3 potentiostat. The measurements were performed using 0.1M Na\(_2\)SO\(_4\) solution at a given bias potential under the dark condition. The measured frequency was 1kHz.

\[
\frac{1}{c^2} = \frac{(E-E_{FB} - kT/e)}{N_0 e \varepsilon_0 \varepsilon} \quad \text{Eq. (1)}
\]

\[
N_d = \frac{2(dE/d(1/c^2))}{e \varepsilon_0 \varepsilon} \quad \text{Eq. (2)}
\]
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References