Supporting Information

Creation of perovskite $LaFeO_3$ network as photoelectrode materials using a salicylate-ligating lanthanum-iron complex precursor

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Contents

Experimental

Chemicals

Methanol (99.9 %), 2-butanol, and triethylamine were used as purchased from Wako. $La(NO_3)_3{\cdot}6H_2O$ and $Fe(NO_3)_3{\cdot}9H_2O$ were purchased from Wako. Hexylsalicylate was used as purchased from Fluka. H_2O (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 $La(NO_3)_3{\cdot}6H_2O$ (0.55 g, 1.27 mmol) and $Fe(NO_3)_3{\cdot}9H_2O$ (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 $LaFeO_3$ crystals using sol-gel method

$LaFeO_3$ crystals were also synthesized for comparison using a reported sol-gel method.[1] $La(NO_3)_3{\cdot}6H_2O$ (5.41 g, 12.5 mmol), $Fe(NO_3)_3{\cdot}9H_2O$ (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_2SO_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 (λ > 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, ε_0, and ε 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.[2] The Mott-Schottky plots were obtained using a VersaSTAT3 potentiostat. The measurements were performed using 0.1M Na_2SO_4 solution at a given bias potential under the dark condition. The measured frequency was 1kHz.

$$1/c^2 = (E-E_{FB} - kT/e)/N_d e\varepsilon_0\varepsilon \quad \text{Eq. (1)}$$

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

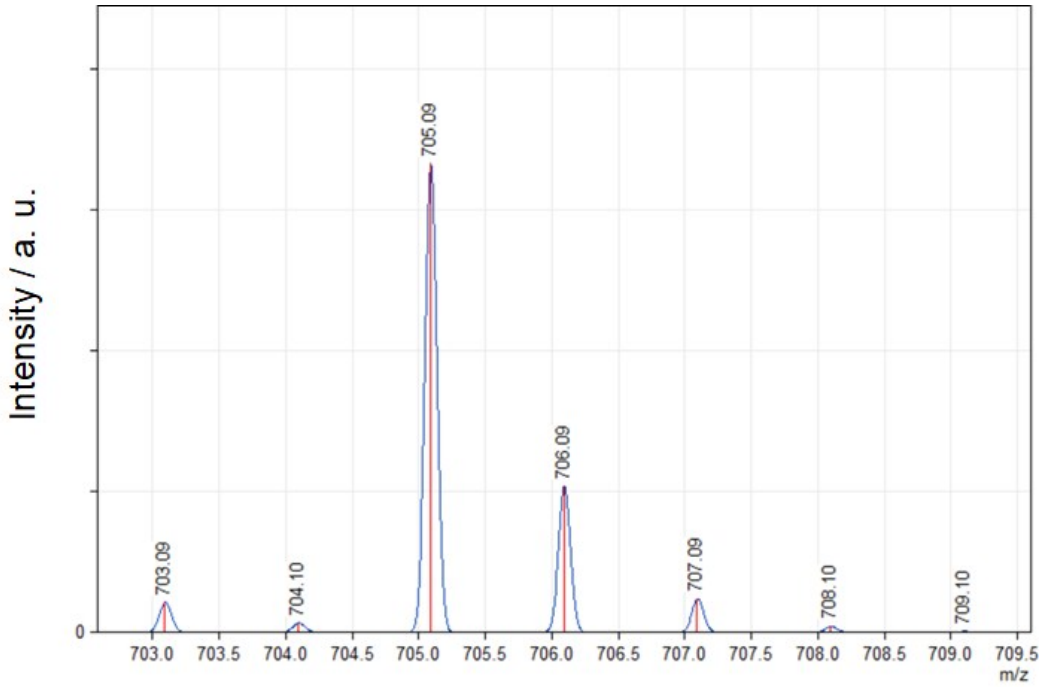

Figure S1: Theoretical isotopic pattern of the ionized species, $[LaFe(O)_2(Hesa)_2(H_2O)_2]$ (with a calculated average m/z of 705.3).

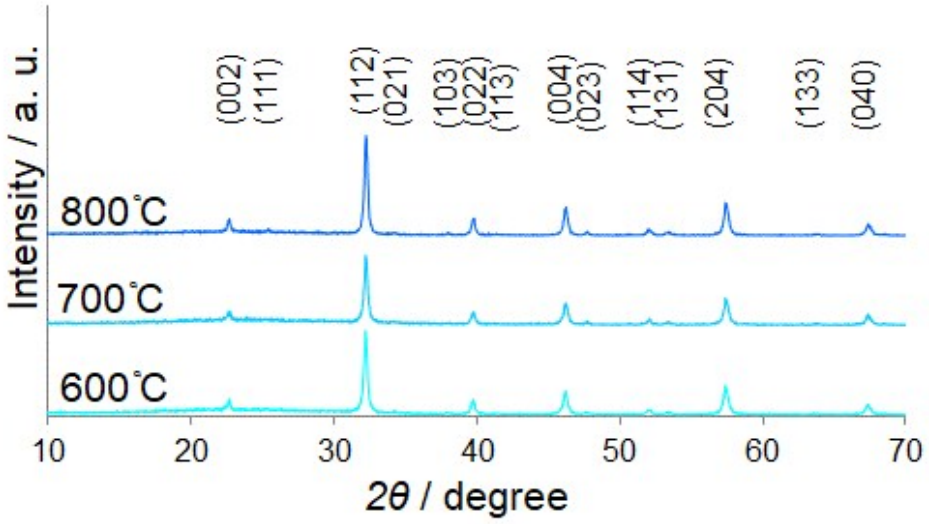

Figure S2: Powder XRD pattern of sol-gel-$LaFeO_3$ samples after sintering at 600–800

°C. The Miller indices corresponding to $LaFeO_3$ (PDF: 01-074-2203) are also shown on

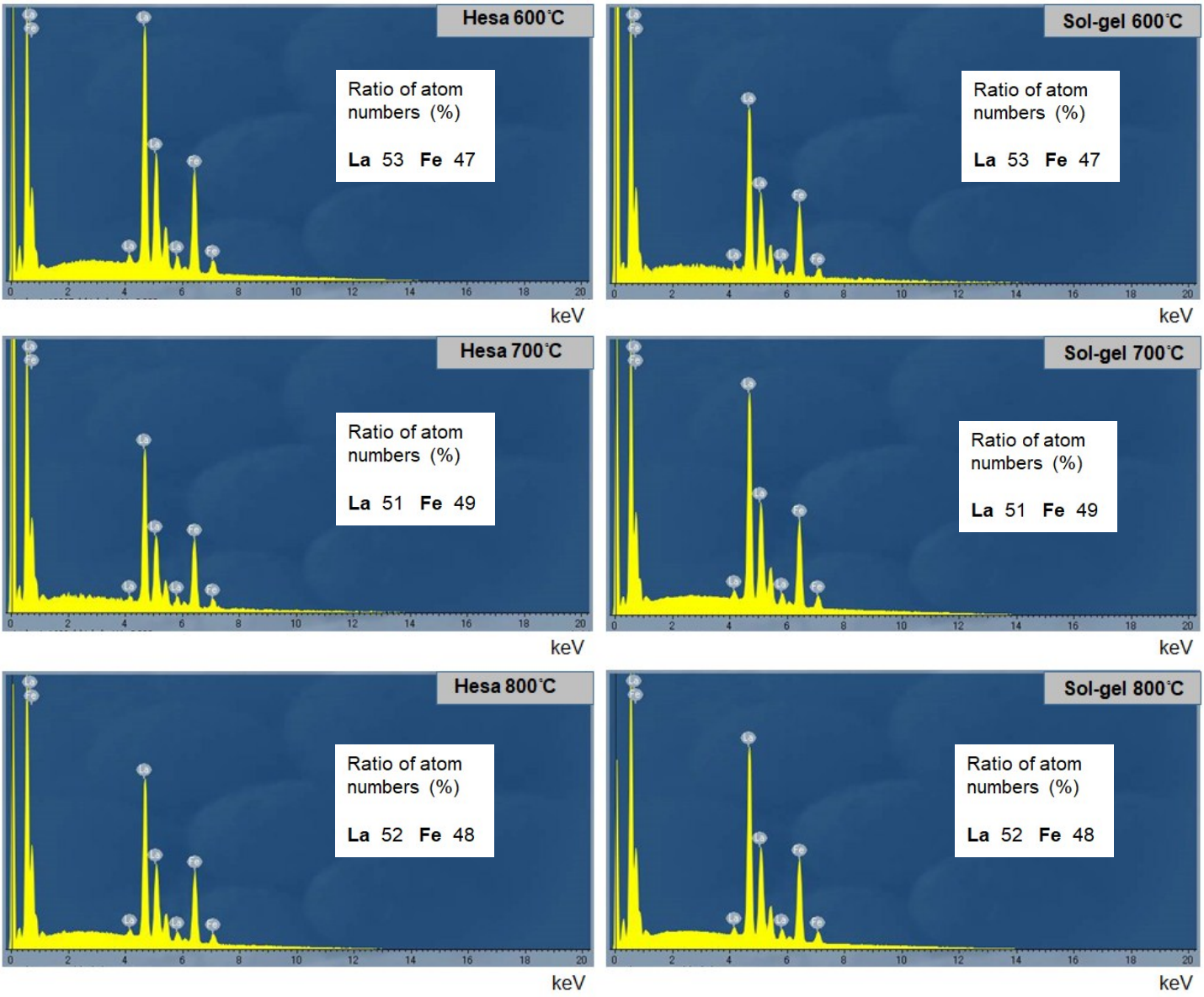

Figure S3: EDX spectra of the obtained $LaFeO_3$ samples. The ratio of atom numbers of La and Fe determined by the EDX are also shown.

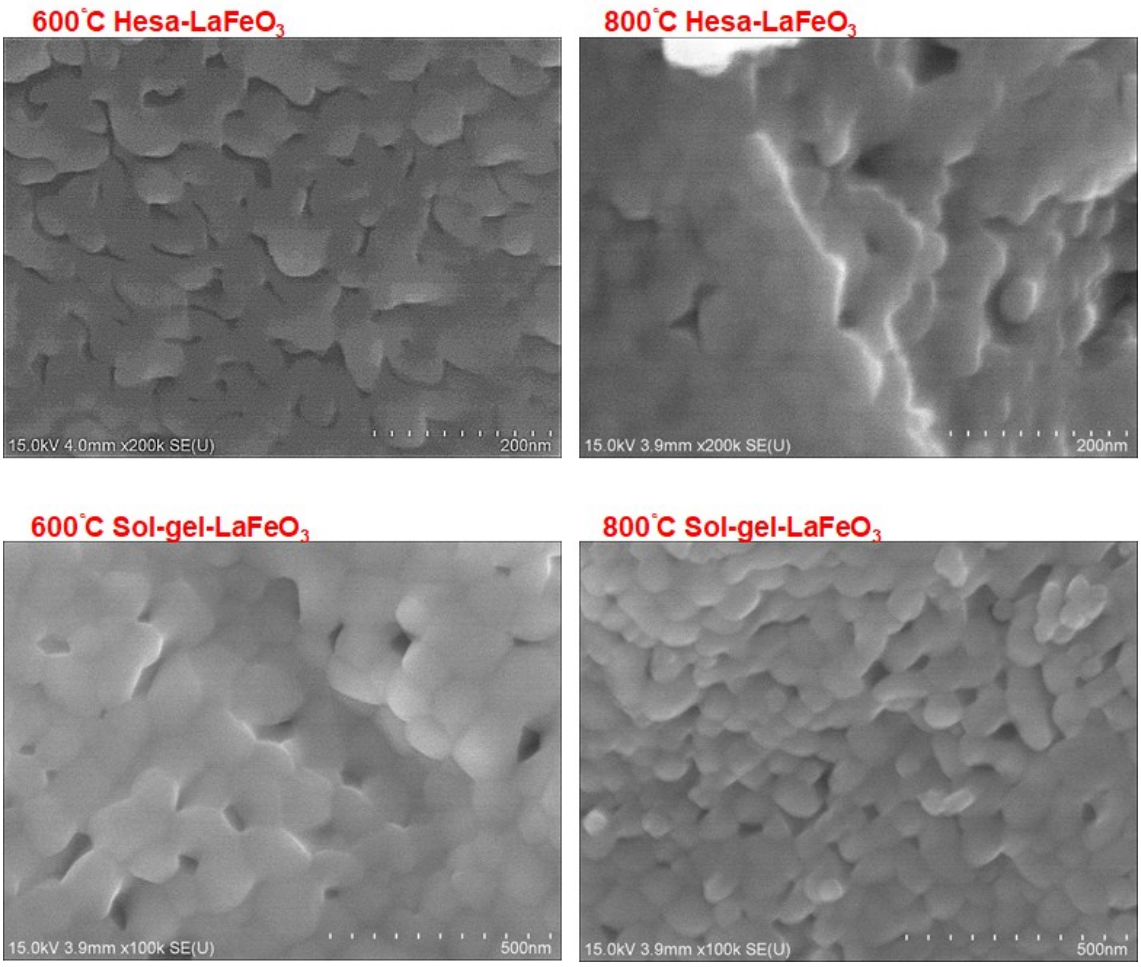

Figure S4: SEM images of Hesa-derived and sol-gel samples after sintering at 600 °C and 800 °C.

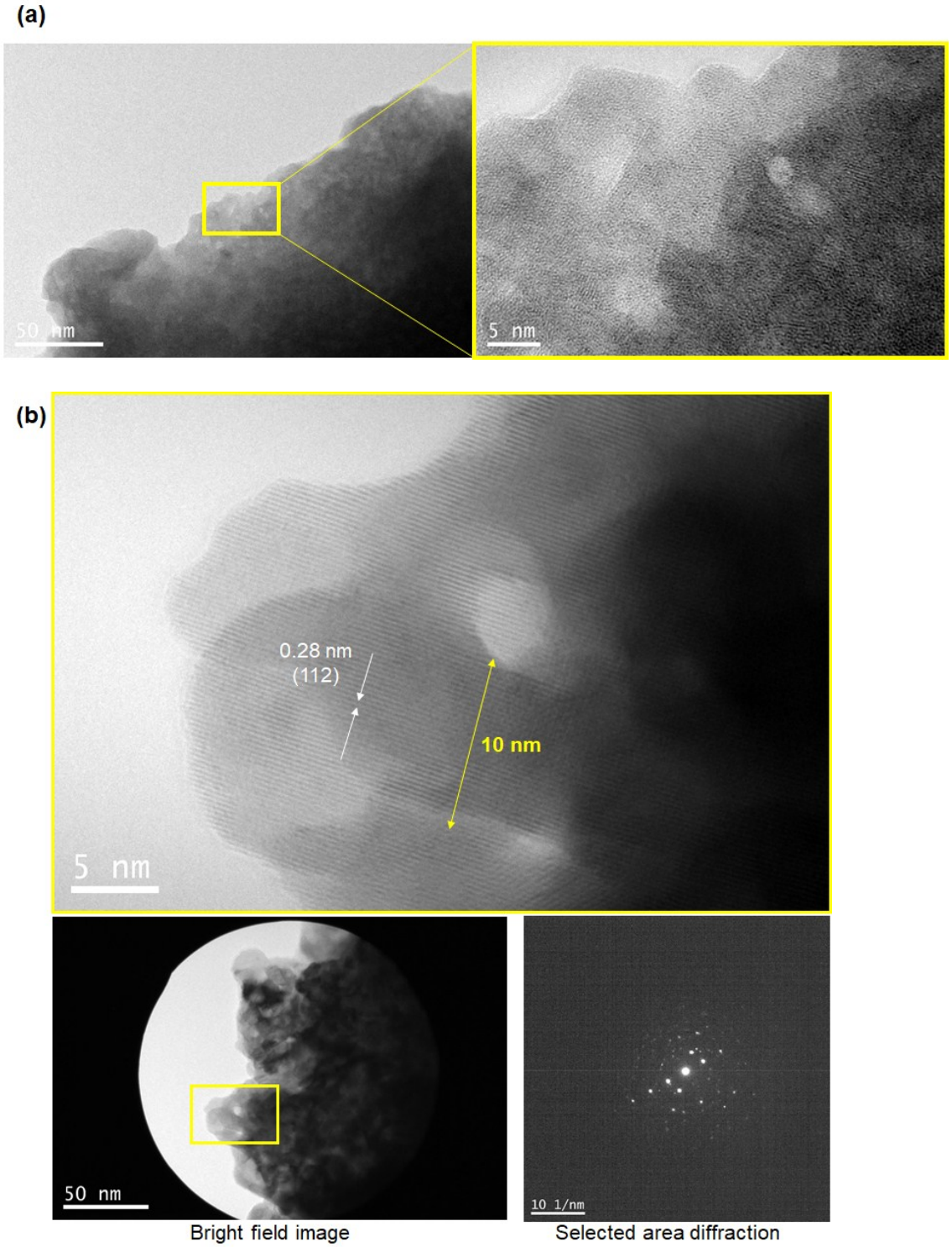

Figure S5: TEM images of $LaFeO_3$ samples obtained by pyrolysis of a salicylate-ligating LaFe complex precursor at (a) 530°C and (b) 580°C. The temperature was

raising from room temperature to 530°C for 1.8 hours and 580°C for 2 hours, respectively, followed by cooling to room temperature.

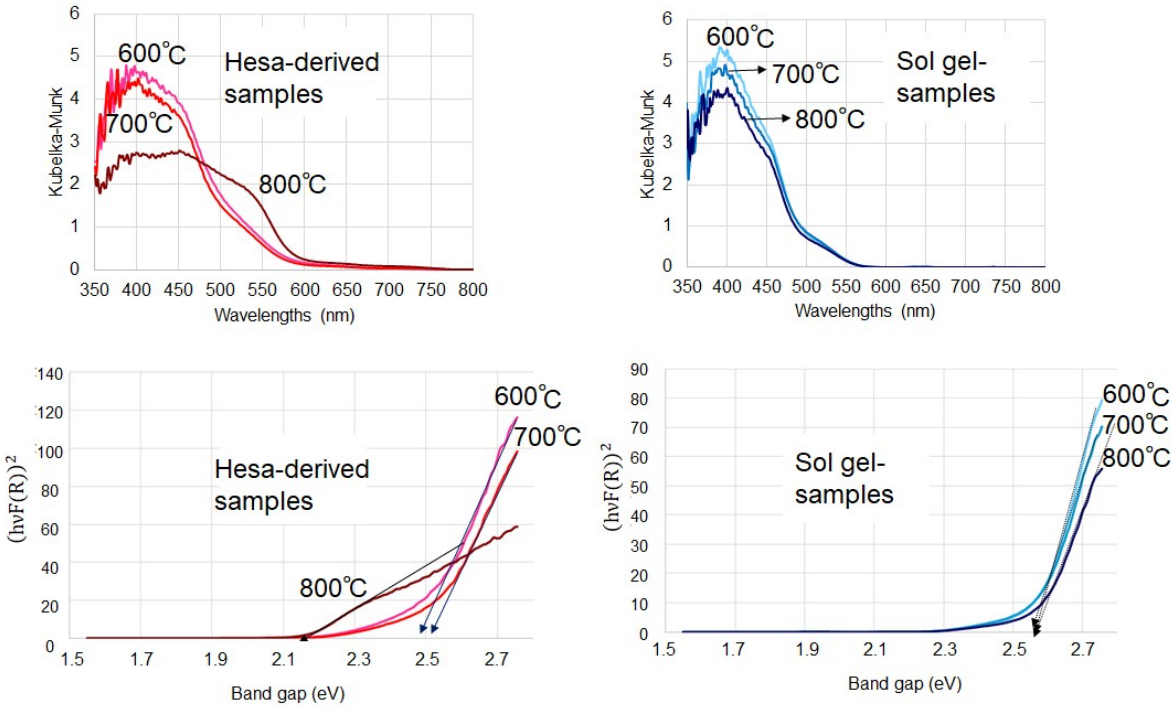

Figure S6: Reflectance spectra of Hesa-derived and sol-gel samples after sintering at 600–800 °C.

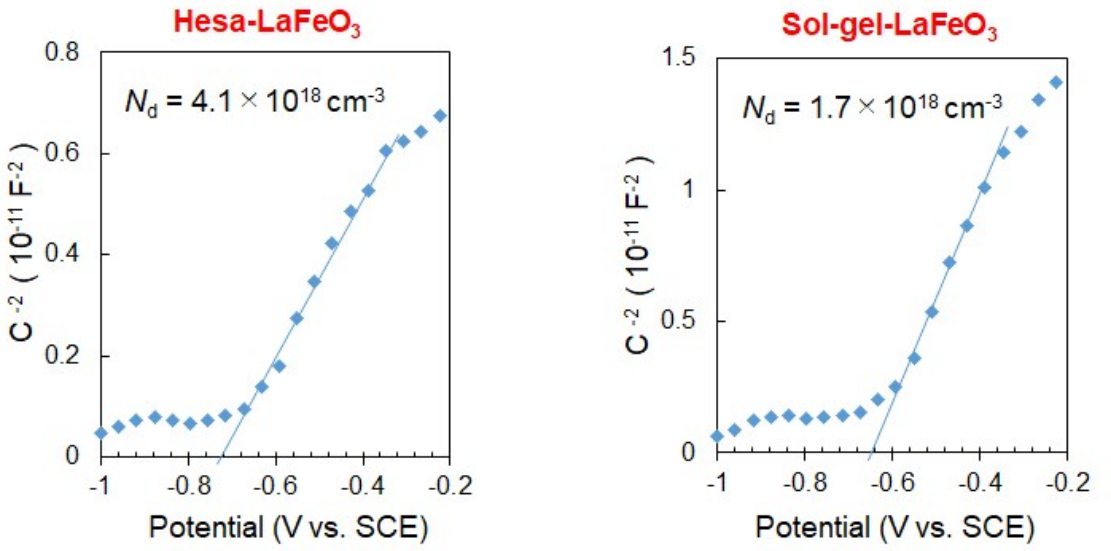

Figure S7: Mott-Schottky plots of Hesa- and sol gel-derived $LaFeO_3$ electrodes for 800 °C samples. Donor densities (N_d) are also presented in the figures.

References

1 K. M. Parida, K. H. Reddy, S. Martha, D. P. Das and N. Biswal, *Int. J. Hydrogen Energy*, 2010, **35**, 12161.

2 Q. Peng, B. Shan, Y. Wen, and R. Chen, *Int. J. Hydrogen Energy*, 2015, **40**, 15423.