Supporting Information

Highly Durable p-$LaFeO_3$/n-Fe_2O_3 Photocell for Effective Water Splitting under Visible Light

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Preparation of $LaFeO_3$ Photocathode

The preparation of $LaFeO_3$ films by PLD includes 3 steps.

Firstly, $LaFeO_3$ powders were prepared by annealing the mixture of La_2O_3 and Fe_2O_3 at 1300°C for 24 hours.

Secondly, $LaFeO_3$ powders were pressed and annealed at 1300°C to form the PLD target. Usually, the size of the target is about 2 cm in diameter with a thickness about 2-3 mm.

Finally, $LaFeO_3$ films were prepared on ITO by PLD using the obtained target. $LaFeO_3$ thin films were prepared by PLD method using a $LaFeO_3$ pellet as the target and ITO as a substrate. $LaFeO_3$ target and ITO substrate were set on the PLD machine (ST-PLD; Pascal co., Japan). The distance between the target and the ITO was set to be 5 cm. Before the laser start to irradiate, pure O_2 was introduced into the chamber until the pressure was researched 4 Pa. When the temperature of ITO substrate researched 650°C, the target was irradiated by laser (Nd:YAG) with wavelength of 355 nm. The frequency and energy of the laser pulse length were fixed on 10 Hz and 62 mJ per pulse, respectively. After the laser irradiation, the film was kept at the same temperature for 30 min in presence of O_2 (160 Pa) as a post-heat treatment.

Characterization

The phase characterizations of samples were carried out by XRD (RIGAKU Rint-2000 X-ray diffractometer). Field-emission scanning electron microscope (JSM-6701 F, JEOL), were used to characterize the morphology of the samples. Optical absorption properties of the $LaFeO_3$ films were measured through an UV–vis spectrophotometer (UV-2500PC; Shimadzu Co., Japan).

PEC Properties

Photocurrent densities curves and Mott-Schottky plots were obtained with an electrochemical station (ALS/CH model 650A) in a three-electrode mode. Platinum and SCE were used as the counter electrode and reference electrode, respectively. AM 1.5 solar simulation (WXS-80C-3 AM 1.5G) with a light intensity of 100 mW cm^{-2} was utilized as the light sources.

Water Splitting

Hydrogen and oxygen generation of the prepared $LaFeO_3$-Fe_2O_3 photocell were measured using a water splitting system. $LaFeO_3$ film with an area of 2 × 2 cm^2 on ITO (2 × 3 cm^2) was set as the photocathode, while Fe_2O_3 film with an area of 1 × 1 cm^2 on ITO (1 × 3 cm^2) was set as the photoanode. 180 ml 1 M NaOH solution was put in a quartz glass cell. Then this glass cell was fixed on the water splitting system which was connected with a closed gas circulation system. The generated H_2 and O_2 were in situ analyzed with a TCD gas chromatograph (Shimadzu GC-8AIT, argon carrier). A 300 W Xe arc lamp (ILC Technology, CERMAX LX-300) was used as the light source. Visible light was realized by using a 300 W Xe lamp with a L42 wavelength cut-off filter. Besides, a water filter is needed between the 300 W Xe lamp and the photocell.

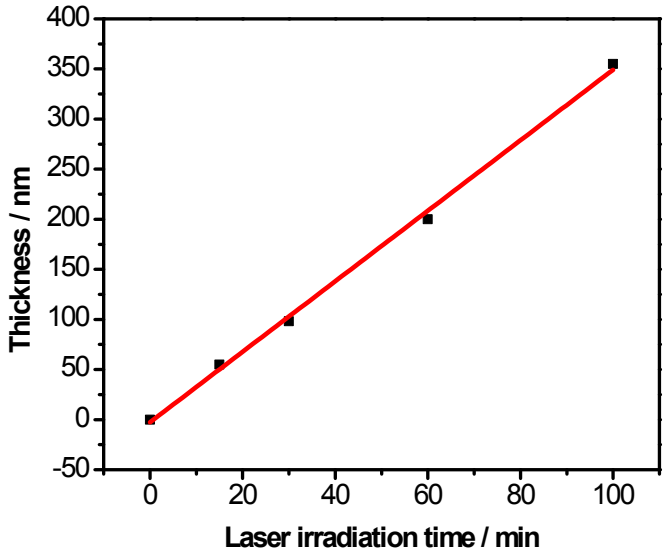

Figure S1. Leaner relationship between thickness of $LaFeO_3$ films and laser irradiation time. The slope is about 3.5 nm/min.

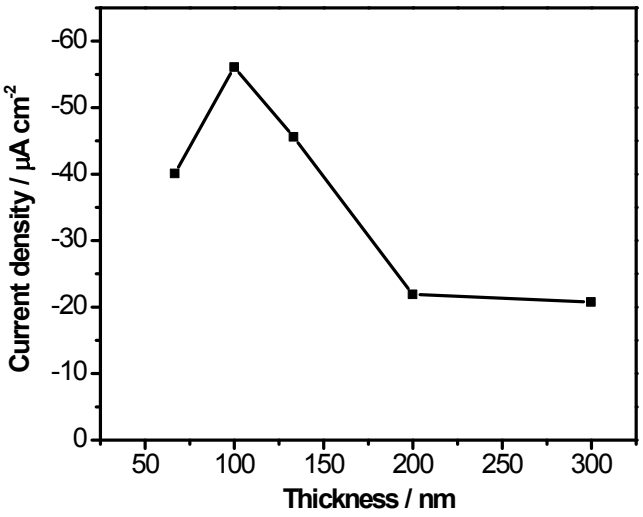

Figure S2. Relationship between current density and thickness of $LaFeO_3$ films in 0.1 M Na_2SO_4 solution at -0.4 V vs. RHE external bias under AM 1.5 solar simulation.

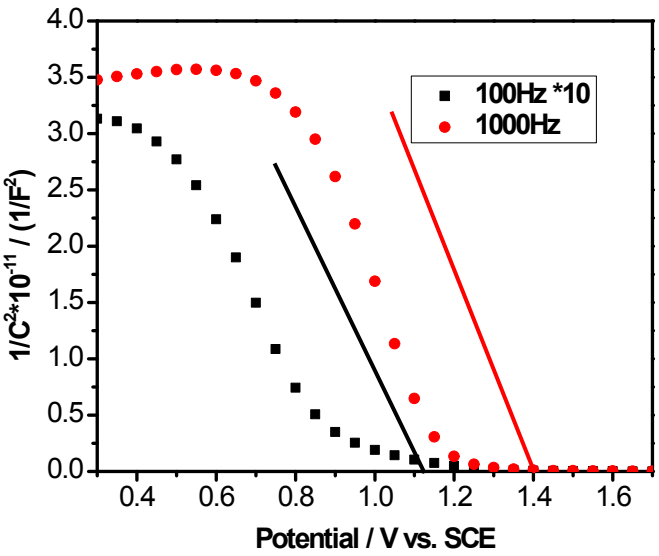

Figure S3. Mott-Schottky plots at 100 Hz and 1000 Hz measured under dark conditions in 0.1M Na_2SO_4 solution

As mentioned in previous manuscript, $LaFeO_3$ exhibits p-type conductivity at high oxygen partial pressures ($P_{O2}>10^{-4}$ atm)[1]. There are cation vacations exist in $LaFeO_3$. When the P_{O2} increases, the population of cation (Fe) vacancies will become significant, and the conductivity will correspond to a material with cation (Fe) vacancies. In this condition, the $LaFeO_3$ will show p-type properties. In the case of our work, the $LaFeO_3$ films were prepared in pure O_2 (4 Pa) atmosphere by PLD. As a result, cation vacancies also exist in the samples and thus p-type $LaFeO_3$ films were obtained.

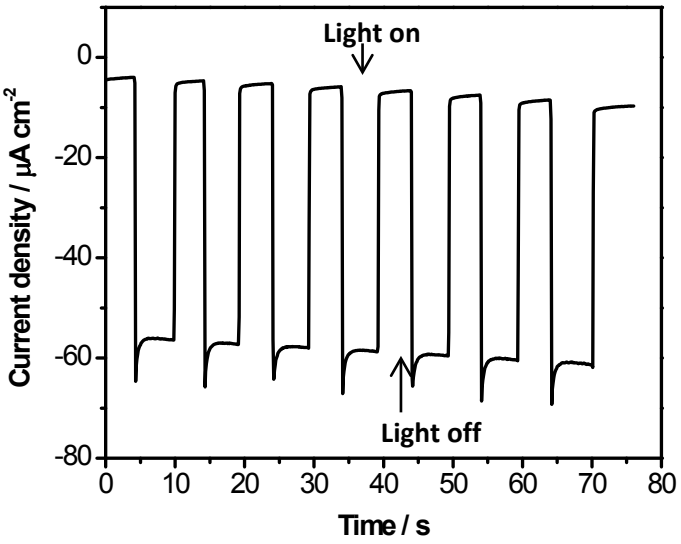

Figure S4. Current-time curves of $LaFeO_3$ photocathodes at 0 V vs. RHE under AM 1.5 illumination (100 mW cm^{-2}) in 0.5 M H_2SO_4 solution.

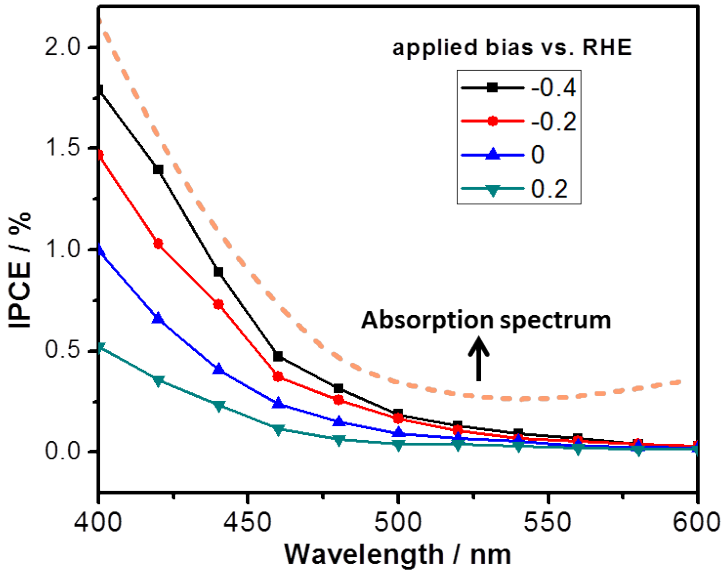

Figure S5. IPCE spectra of $LaFeO_3$ photocathodes at 0.2 V, 0 V, -0.2 V and -0.4 V vs. RHE applied potential in 1 M NaOH solution. The dot curve is the absorption spectra of $LaFeO_3$ photocathodes.

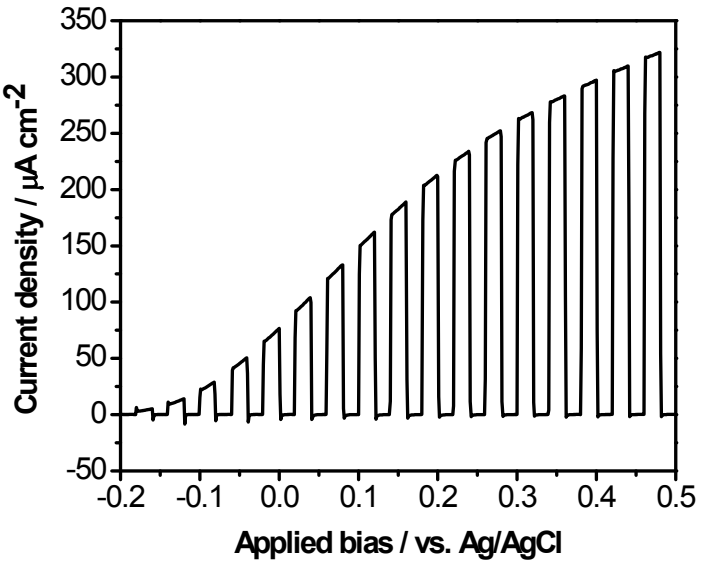

Figure S6. Current-potential curves of Fe_2O_3 photoanodes in 1 M NaOH solution under AM 1.5 illumination.

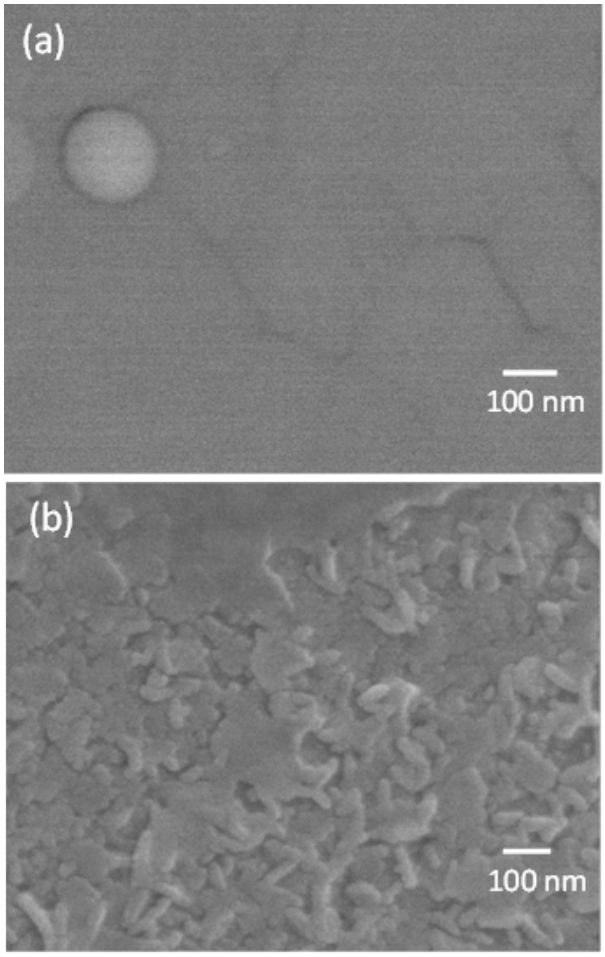

Figure S7. SEM images of $LaFeO_3$ films before (a) and after (b) 30 hours under visible light irradiation. The external bias is -1.5 V.

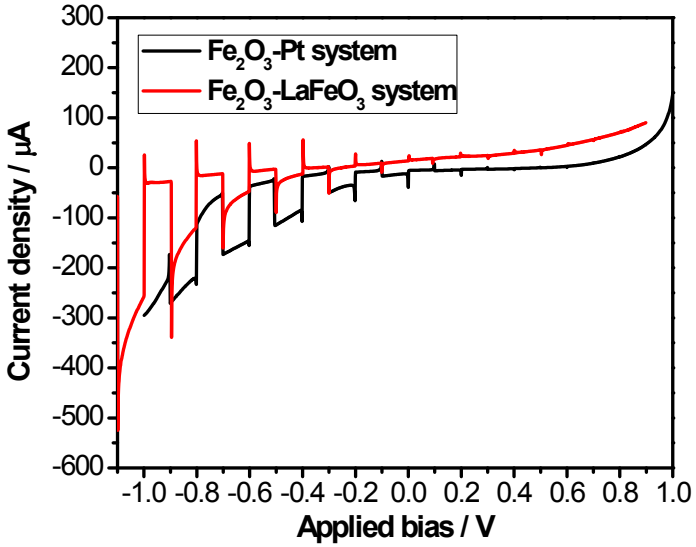

Figure S8. Current-potential curves of Fe_2O_3/Pt (black line) and Fe_2O_3/$LaFeO_3$ (red line) respectively in 1 M NaOH solution under AM 1.5 illumination in two electrode system.

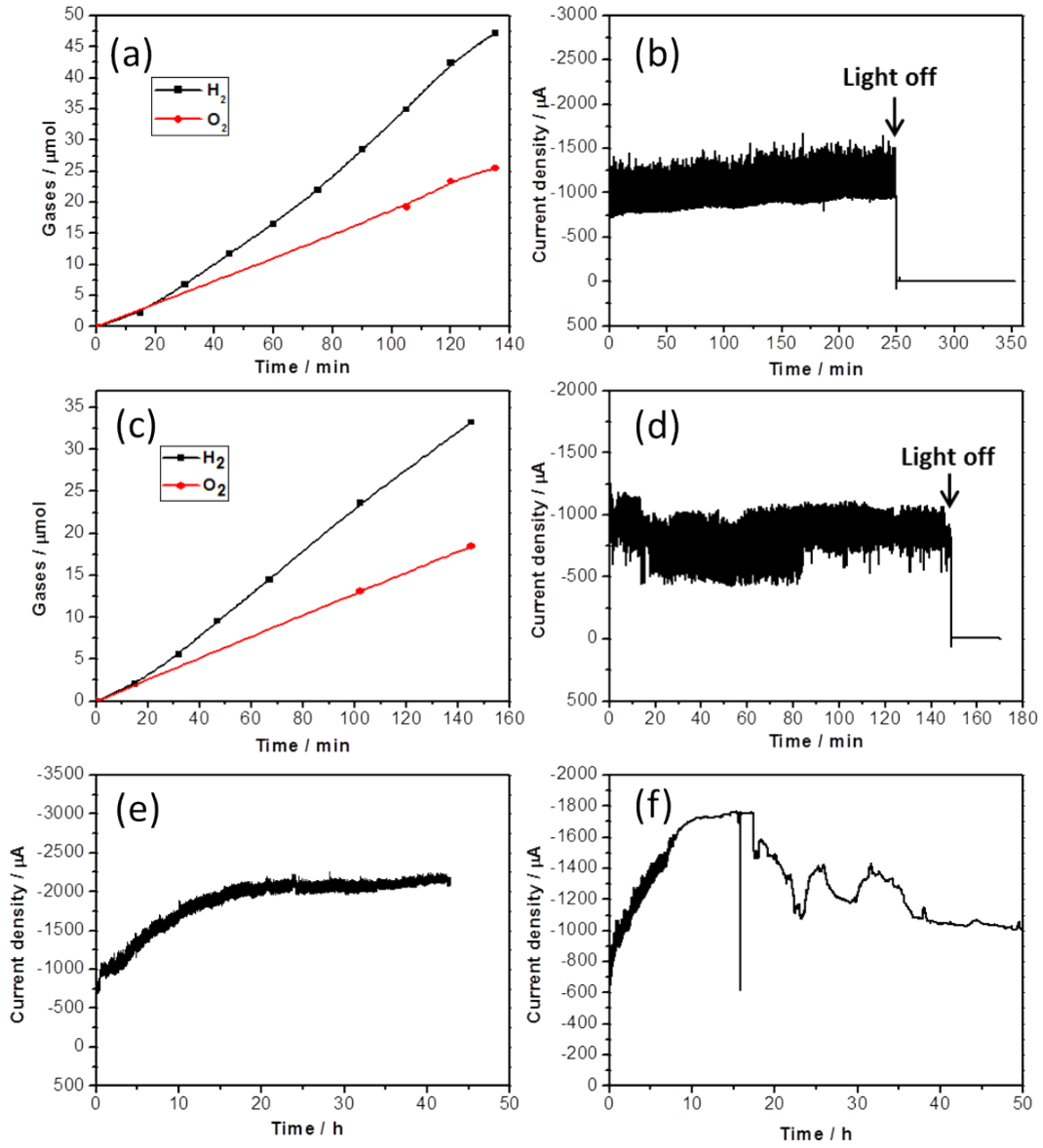

Figure S9. Time courses of gas evolution for the $LaFeO_3/Fe_2O_3$ (a) and Fe_2O_3/Pt (c) under UV-vis light irradiation. (b) and (d) are corresponding current-time curves. The external bias is -1.0 V. (e) and (f) are current-time curves at -1.5V external bias for $LaFeO_3/Fe_2O_3$ (e) and Fe_2O_3/Pt (f) respectively.

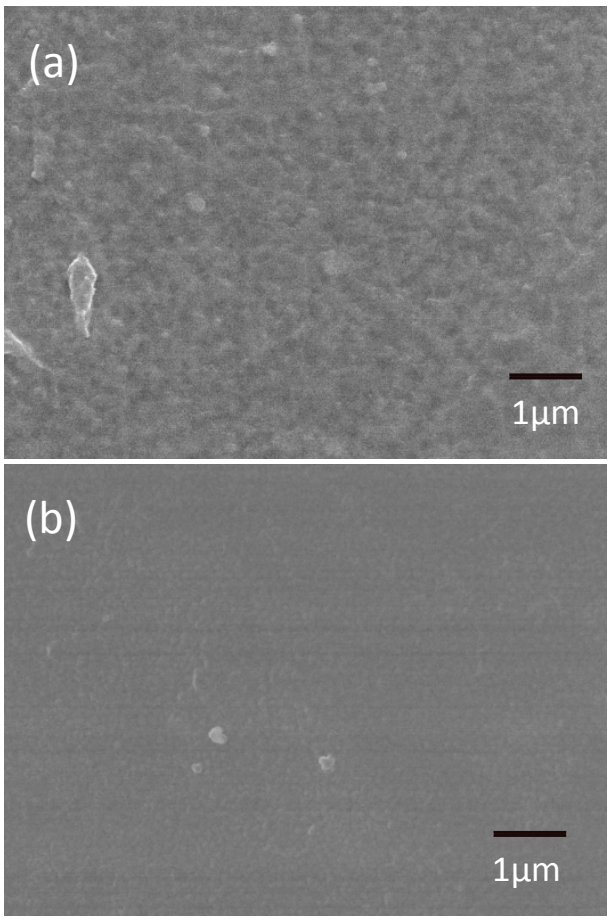

Figure S10. SEM images of $LaFeO_3$ photocathode (a) and Fe_2O_3 photoanode (b) after 120 hours under visible light irradiation. The external bias is -1.2V.

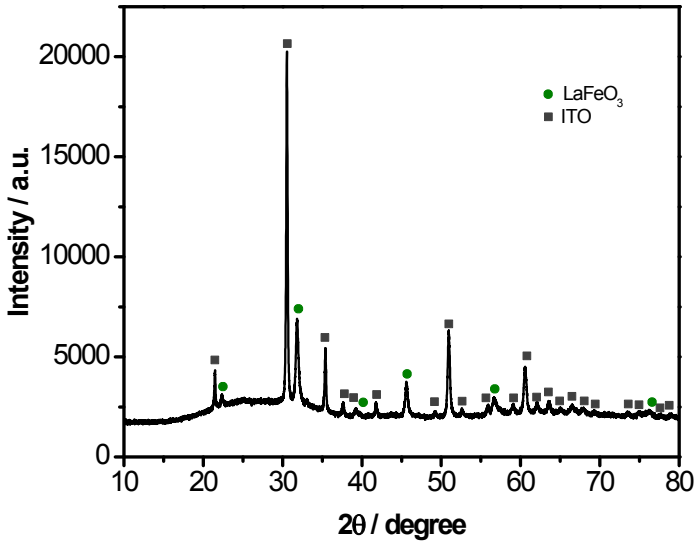

Figure S11. XRD patterns of $LaFeO_3$ photocathodes after water splitting under visible light irradiation for 120 hours. The external bias is -1.2V.

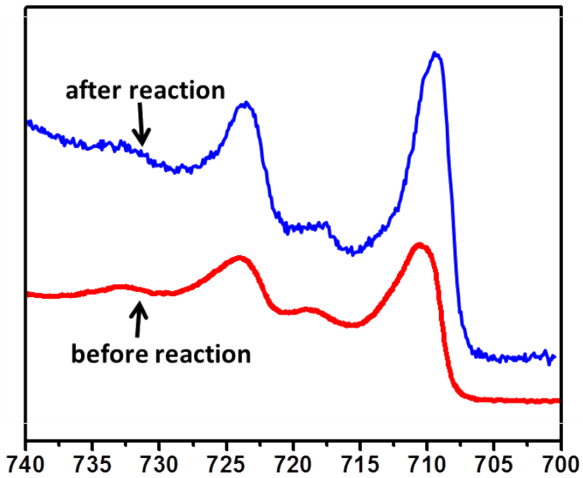

Figure S12. XPS spectras of Fe (2p) in $LaFeO_3$ photocathodes before and after water splitting under visible light irradiation for 120 hours. The external bias is -1.2V.

References:

[1] I. Waernhus, P. E. Vullum, R. Holmestad, T. Grande, K. Wiik, Solid State Ionics 2005, 176, 2783