Electronic Supplementary Material (ESI) for ChemComm.

Insight into the Enhanced Photoelectrocatalytic Activity in the Reduced $LaFeO_3$ Films

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1. Experimental section

1.1 Preparation of LFO target

Mixtures of equimolar La_2O_3 and Fe_2O_3 were annealed at 1300°C for 24 hours to obtain the $LaFeO_3$ powders. After confirming its purity by XRD in ESI, $LaFeO_3$ powders were pressed under 10Mpa for 0.5 hour and annealed at 1300°C to form the PLD target. And the dense target is about 1 inch in diameter with a thickness of 3 mm[1].

1.2 Deposition of LFO films

The single crystal (001)-oriented $SrTiO_3$ substrates, 1×1 cm in size, were degreased in acetone and ethanol. Then cleaned substrates were soaked in pure water for 30 min in ultrasonic bath. The excessive strontium oxide or hydroxide composites segregated on the $SrTiO_3$ surface were etched by a dilute HF solution (5%) for 15 sec. And these STO were immediately rinsed by pure water[2]. Finally, LFO films were prepared by PLD with a 248 nm KrF excimer laser operating at the energy density of 1.5 J/cm^2 on the target surface and the frequency of 6 Hz.

After the substrate stabilized at 750 °C, pure O_2 with a flow rate of 50 ccm was introduced into the vacuum chamber and the pressure researched 75 Torr. $LaFeO_3$ target was cleaned for 1000 pulses with the shutter closed and the substrate was set to be 1 cm higher than the visible plasma plume. Deposition of the LFO films with the thickness of 100nm started with shutter opened for 20000 pulses. After that, the film was kept at the same temperature for 30 min in different O_2 pressure (4×10^{-4}, 4×10^{-2}, 4×10^{0}, 4×10^{2} Torr) to tune the crystal and electron structure.

1.3 Characterization

Powders XRD (Rigaku D/MAX2550) was used to confirm the purity of $LaFeO_3$ powders by solid-phase synthesis. Oxygen vacancies have been confirmed by electron spin resonance (JEOL JES-FA200) with a microwave frequency of 9.4GHz at 15mW. Lattice constant of the films, depended on oxygen vacancy concentration, was checked by high-resolution XRD (Rigaku Ultima Ⅳ) and rocking curve was used to show their crystalline quality. Surface morphologies were analyzed with SEM by FEI

Helios Nanolab 600i. The UV−Vis absorption spectrum within the wavelength 200~850 nm was obtained with Shimadzu U-4100. Photoluminescence spectra were collected with an excitation wavelength of 290nm by Edinburgh FLS 920. And PL lifetime at the emission wavelength of 467nm was obtained by a statistics of 10000 PL counts. Binding energies of core level were collected on a Thermo ESCALAB250 XPS with the Al Kα (1486.6 eV) as the X-ray excitation source. XPS scanned the valence band spectrum to study the electronic structure near the Fermi level. LSV at a scan rate of 5mV/s from 0.3 V to 1.4 V was used to study the oxygen evolution reaction on a CHI 802D electrochemical workstation in three-electrode system (Work electrode: LFO films, Reference electrode: Ag/AgCl, Counter electrode: platinum). And photoelectrocatalysis reacted in 0.1M KOH electrolyte bubbled with O_2 under irradiation from a 300W Xe arc lamp. Electrochemical impedance spectroscopy (EIS) was used to compare the electrical conductivity of LFO films at 0.85V vs. Ag/AgCl with a frequency range of 0.1Hz~100kHz.

2. Supporting figures

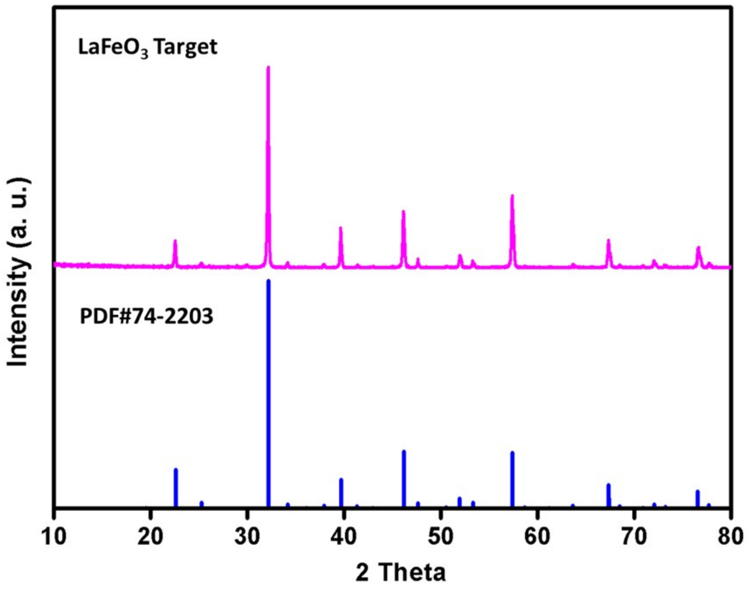

Figure 1. Powders XRD of LaFeO$_3$ target for PLD.

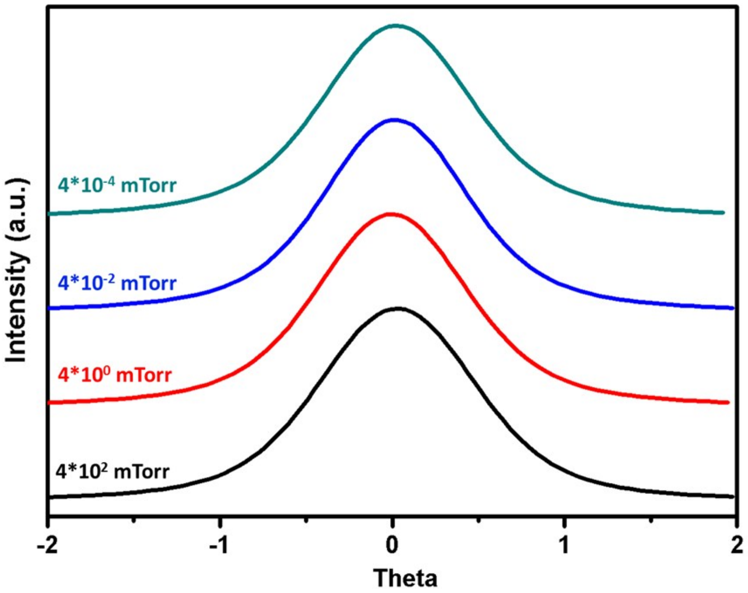

Figure 2. Rocking curves of LFO films annealed in different oxygen pressure. Similar full width at half maxium means similar crystal quality.

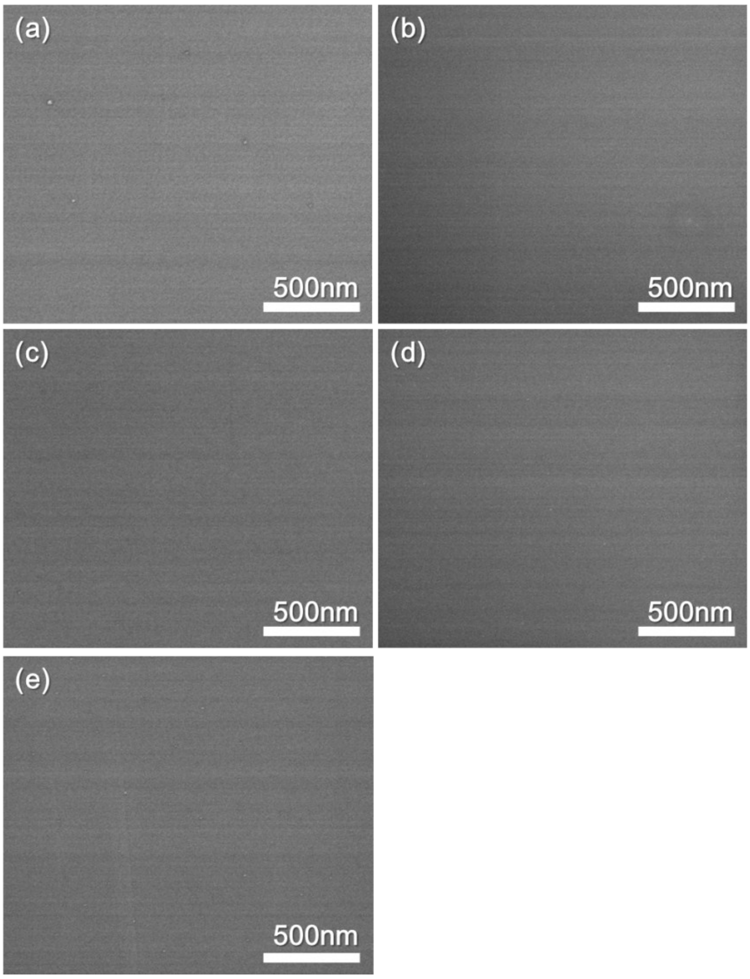

Figure 3. SEM of LFO films annealed in different oxygen pressure: (a) 4×10^{-4}, (b) 4×10^{-2}, (c) 4×10^{0}, (d) 4×10^{2} Torr, (e) without annealing process.

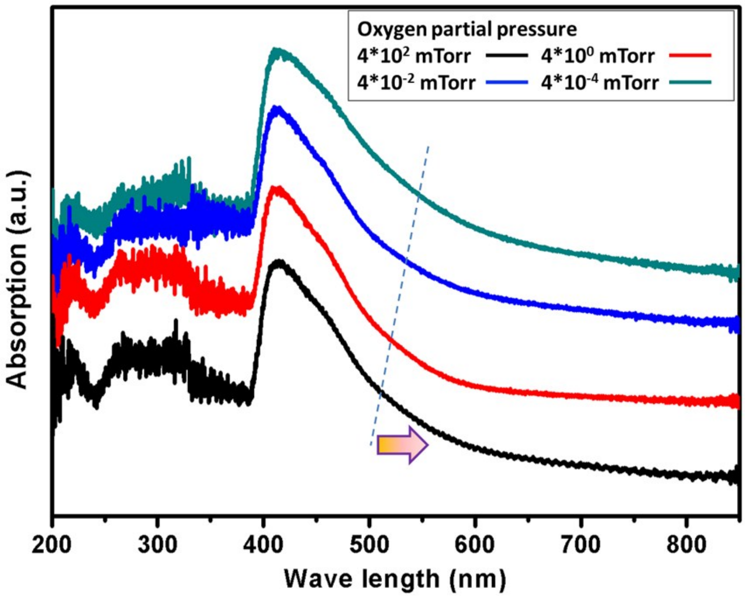

Figure 4. UV−Vis absorption spectrum of LFO films annealed in different oxygen pressure.

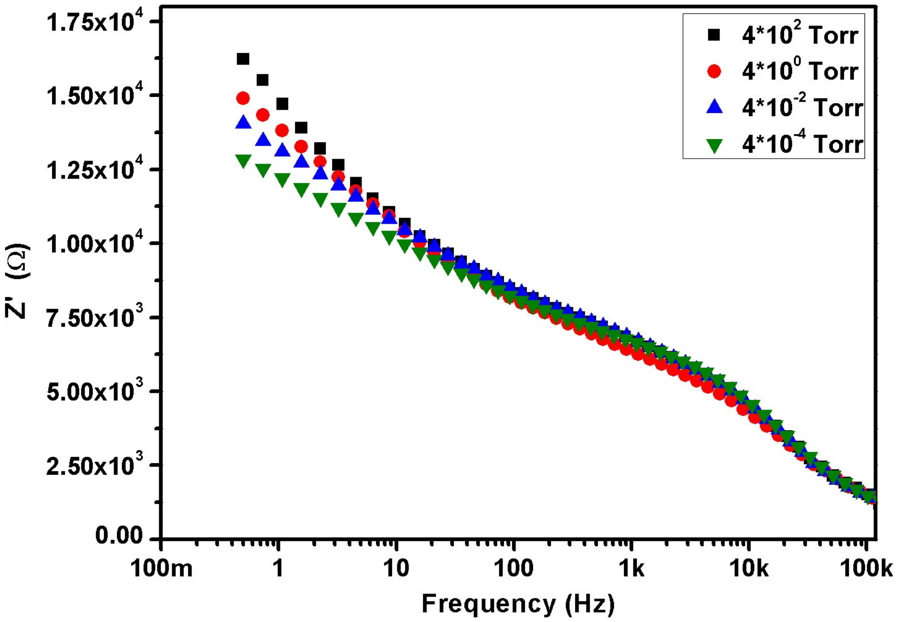

Figure 5. EIS of LFO films annealed in different oxygen pressure.

References

1. Q. Yu, X. Meng, T. Wang, P. Li, L. Liu, K. Chang, G. Liu and J. Ye, *Chem. Comm.*, **2015**, 51, 3630-3633.
2. (a) Y. Tsuchiya, K. Norota, Y. Watabe, T. Kuroda, N. Iwata, T. Hashimoto and H. Yamamoto, *Trans. Mat. Res. Soc. Japan*, **2012**, 37, 369-372; (b) J. Connell, B. Isaac, G. Ekanayake, D. Strachan and S. Seo, *Appl. Phys. Lett.*, **2012**, 101, 251607.