Supporting Information

Engineering surface of perovskite $La_{0.5}Sr_{0.5}MnO_3$ for catalytic activity of CO oxidation

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Synthesis

$La_{0.5}Sr_{0.5}MnO_3$ was synthesized by traditional hydrothermal method. The initial solutions were first made, such as $La(NO_3)_3$ (0.40 M), $Sr(NO_3)_2$ (0.40 M), $KMnO_4$ (0.36 M) and $MnCl_2$ (0.56 M). In a typical procedure of the synthesis, 17.5 mL $La(NO_3)_3$, 17.5 mL $Sr(NO_3)_2$ and 9 mL $KMnO_4$ were mixed on stirring, 40 g KOH were added into the solution slowly to avoid vigorous reaction. 18.3 mL $MnCl_2$ were add in droplet way to make a reaction solution. The solution was transferred into a stainless steel lined Teflon vessel (95 mL in volume) for hydrothermal treatment at 260 °C for 48 h. After natural cooled to room temperature, products were washed with deionized water and dried at 60 °C in air.

Dilute HNO_3 activation

Less than 1 g of $La_{0.5}Sr_{0.5}MnO_3$ was added to a dilute 240 mL HNO_3 (3.0 M) solution while maintaining the solution pH. The time of treatment is 6 min and 60 min, respectively. After the acid treatment, the solution was decanted and washed with extra amount of deionized H_2O and dried at 60 °C in air.

Characterization

The powder XRD patterns of products were collected on a Rigaku D/Max 2550 VPC diffractometer with Cu Kα radiation (λ = 0.15418 nm) of 50 kV and 200 mA at room temperature by step scanning in an angle rang of 20° $\leqslant 2\theta \leqslant$ 80° and increments of 0.02 ° were employed. Scanning electron microscope (SEM) images were graphed with a Helios NanoLab 600i Dual Beam System, FEI Company, with an EDS equipment (EDAX) from Ametek Company. Product compositions were determined by inductively coupled plasma spectroscopy (Thermo, iCAP 6300). Characterization of the BET surface area of the samples was carried out with a Micromeritics ASAP 2020 apparatus. Nitrogen adsorption-desorption isotherms were carried out with a Micromeritics ASAP 2420 nitrogen adsorption apparatus at 77 K. The pore size distribution plots were obtained by the Barret-Joyner-Halenda (BJH) model. The BET specific surface areas were (a) 0.36 m^2g^{-1}, (b) 5.90 m^2g^{-1} and (c) 20.22 m^2g^{-1} for sample 1#, 2#, 3#, respectively.

X-ray photoemission (XPS) measurements were carried out using a Thermo Fisher Scientific ESCALAB 250 with photoelectron spectroscopy system using a 300W monochromatic Al Kα (1486.6 eV) X-ray source. The instrument work function was calibrated to given an Au $4f_{7/2}$ metallic gold binding energy

(BE) of 83.96 eV. The spectrometer dispersion was adjusted to give a BE of 368.21 eV for metallic $Ag3d_{5/2}$ and 932.62 eV for metallic $Cu2p_{3/2}$. The XPS spectra were collected in constant analyzer energy (CAE) mode. Instrument base pressure was 2.0×10^{-10} mbar and high-resolution spectra were collected using a spot size of 500 μm, with pass energy of 20 eV and with a 0.05 eV/step. The pass energy correspond to an Ag $3d_{5/2}$ FWHM of 0.60 eV. The charge neutralization being monitored using the C 1s (284.6 eV) signal for adventitious carbon, all samples were monitored within ±0.2 eV for surface charge was neutralized using Ag paint by conduct with sample holder.

The atomic concentration of La, Sr and Mn has been calculated from narrow scan of La3d, Sr3d and Mn2p using software of Avantage Data system. When data is quantified, the peak areas are measured with Shirley background type, suitable sensitivity factors are applied to the data and a correction for the instrument transmission function is made. The instrument transmission function is calculated from a polynomial fit to experimental data, based on the kinetic energy of the peak, pass energy, X-ray spot size or source and Lens Mode.

Evaluation of catalytic performances of catalysts

Activity measurements were performed in a fixed-bed quartz reactor (inner diameter of 5 mm) using 100 mg of the catalyst measuring 40-60 mesh. The feed gas mixture contained 2000 ppm CO, 10 % O_2, and the balance gas was N_2. The total flow rate of the feed gas was 200 $cm^3 \cdot min^{-1}$. The concentrations of the CO were continually monitored by an FTIR spectrometer (MultiGas TM 2030 FTIR Continuous Gas Analyzer). The conversions of CO were defined as (cinlet-coulet)/cinlet 100 %, where the cinlet and coutlet were the CO concentration of inlet and outlet feed stream, respectively. For H_2-TPR test, the samples were heated under a 10 % H_2/Ar gas flow (50 $cm^3 \cdot min^{-1}$) at a rate of 10 °C•min^{-1} up to 1000 °C.

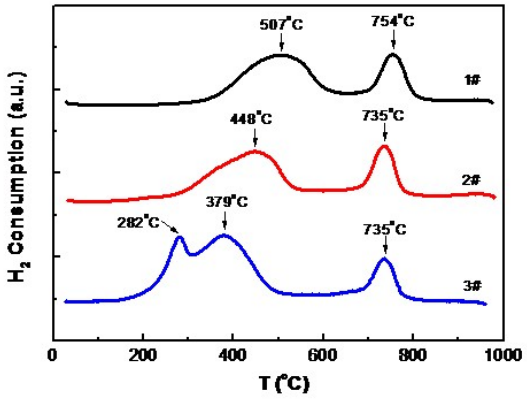

Fig. S1 H_2 temperature program reduction of as-prepared samples (without treatment (1#), and

treated with dilute nitric acid solution for 6 min (2#) and 60 min (3#)).

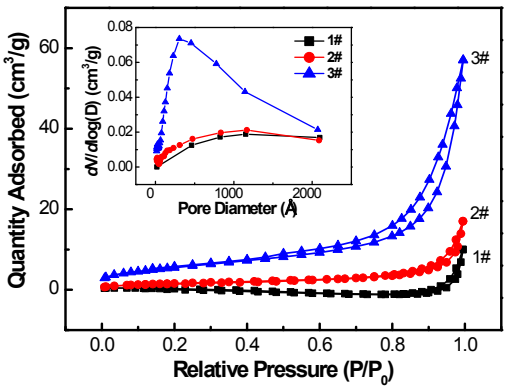

Fig. S2 Nitrogen adsorption-desorption isotherms of $La_{0.5}Sr_{0.5}MnO_3$ (without treatment (1#), and treated with dilute nitric acid solution for 6 min (2#) and 60 min (3#)).

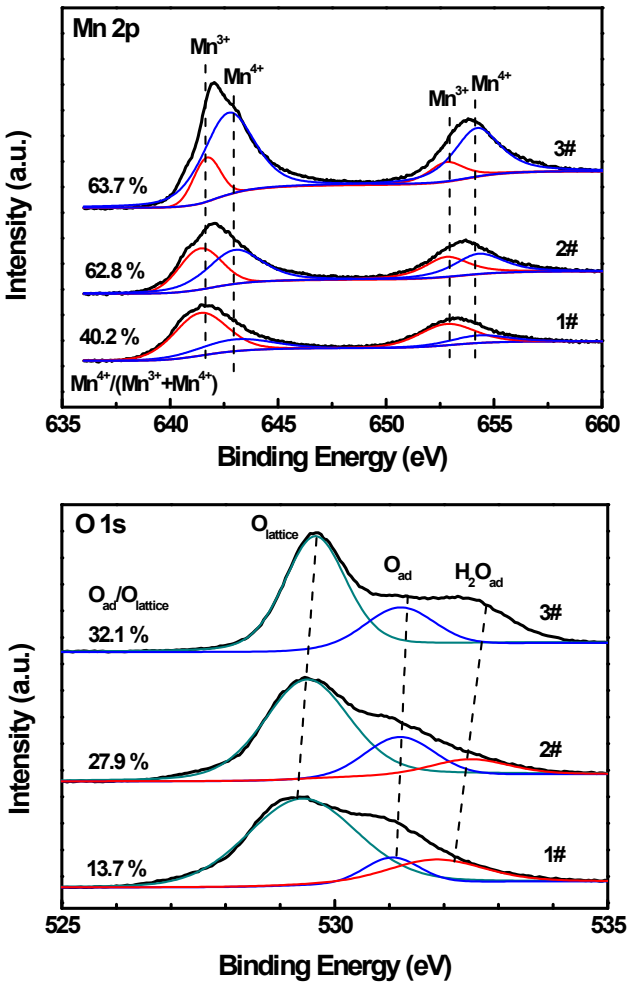

Fig. S3 The Mn 2p (a) and O 1s (b) XPS spectra of different duration (without treatment (1#), and treated with dilute nitric acid solution for 6 min (2#) and 60 min (3#)) of activation $La_{0.5}Sr_{0.5}MnO_3$.

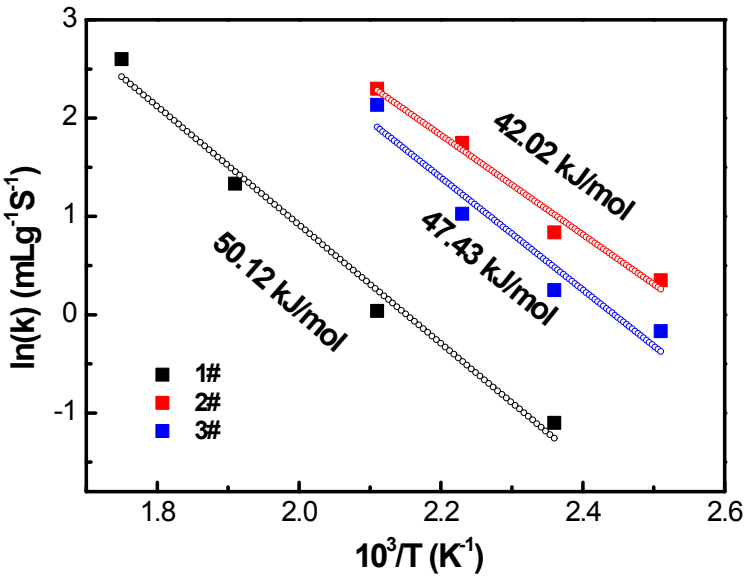

Fig. S4 Arrhenius plots for CO oxidation over the $La_{0.5}Sr_{0.5}MnO_3$ samples (without treatment (1#), and treated with dilute nitric acid solution for 6 min (2#) and 60 min (3#)).