Supporting Information

Green Catalyst: Magnetic $La_{0.7}Sr_{0.3}MnO_3$ Hollow Microspheres

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1. Experimental section

1.1. Regents

Lanthanum nitrate hexahydrate ($La(NO_3)_3 \cdot 6H_2O$, AR)，strontiumnitrate ($Sr(NO_3)_2$, AR), manganese acetate tetrahydrate ($Mn(CH_3COO)_2 \cdot 4H_2O$, AR), polyvinylpyrrolidone (PVP-K30, AR) and N,N-dimethylformamide (DMF, AR) were purchased from Sinopharm Chemical Reagent Co. Ltd. All chemicals were used without further purification.

1.2. Preparation of the precursor solution

In the typical experiment, 4 mmol stoichiometric amount of $La(NO_3)_3 \cdot 6H_2O$, $Sr(NO_3)_2$, $Mn(CH_3COO)_2 \cdot 4H_2O$ and 1.5381 g polyvinylpyrrolidone (PVP) were mixed in 5 mL N,N-dimethylformamide (DMF). Then the mixture was stirred till the solution became homogeneous.

1.3. Preparation of LSMO hollow spheres

The final homogeneous mixture was loaded into a plastic syringe. The needle tip was connected with a terminal while aluminum foil covering collector worked as counter electrode. The applied voltage was 15 kV at a constant distance of 13 cm between the tip and collector under a flow rate of 0.15 ml/h with a needle of inner diameter of 0.34 mm. The obtained LSMO/PVP composites were dried at 60 ^oC for 12 h and calcined at 1 ^oC/min, 5 ^oC/min and 10 ^oC/min under 650 ^oC for 5 h in air.

1.4. Preparation of LSMO nanoparticles

The same homogeneous mixture as that used in electrospinning process was dried at 60 ^oC for 12 h and calcined at 1 ^oC/min, 5 ^oC/min and 10 ^oC/min under 650 ^oC for 5 h in air.

1.5. Characterization of LSMO hollow spheres

Power X-ray diffraction (XRD) patterns were obtained using a Rigaku D/Max 2550 V/PC X-ray diffractometer with Cu Kα radiation (λ=1.54718 Å) operating at 50 kV and 200 mA at room temperature by step scanning in the angle range of $20^o \leq 2\theta \leq 80^o$ with an increment of 0.02 °. Inductively coupled plasma spectroscopy (ICP) was used to determine the composition of products. Scanning electron microscope (SEM) with a Helios NanoLab 600i Dual Beam System from FEI Company, was employed to observe the morphology of products. The high-resolution transmission electron microscopy (HRTEM) image was obtained using an electron microscope (Tecnai F20) operated at 200 kV from FEI Company. The X-ray photoelectron spectra (XPS) was taken on a Thermo ESCALAB 250Xi electron energy spectrometer using Al Kα (1486.6 eV) as the X-ray excitation source. Nitrogen adsorption-desorption isotherms were collected from a TriStar 3000 (Micromeritics) nitrogen adsorption apparatus at 77 K. The magnetic properties were investigated with a superconducting quantum interference device (SQUID) magnetometer (Quantum Design) from 4 to 380 K.

1.6. Photocatalytic Water Oxidation

The photocatalytic water evolution was performed in a 20 mL sodium bicarbonate solution (1 mM, adjust to pH=7.0 with H_2SO_4) containing 250 ppm catalyst, $Na_2S_2O_8$ (10.0 mM) as an electron acceptor, and $[Ru(bpy)_3]Cl_2$ (0.5 mM) as a photosensitizer. The solution was purged with N_2 gas for 10 min in a reactor and then sealed with a quartz cover. The reaction was started by irradiating the solution with a Newport oriel sol3A solar simulator through a transmitting glass filter ($\lambda > 420$ nm) with magnetic stirring at room temperature. Dissolved O_2 concentration was measured with a Clark type electrode.

2. Figures

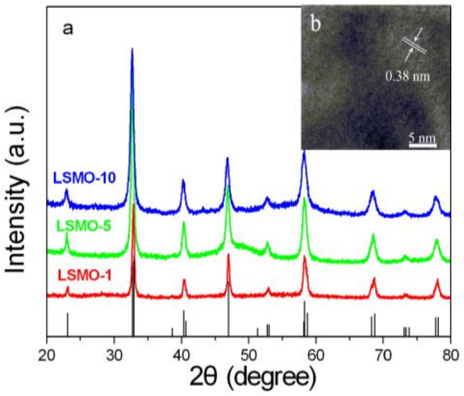

Fig. S1. (a) Power XRD patterns of LSMO microspheres and reference of JCPDS card No. 51-0409, (b) cross-sectional HR-TEM image of LSMO-10.

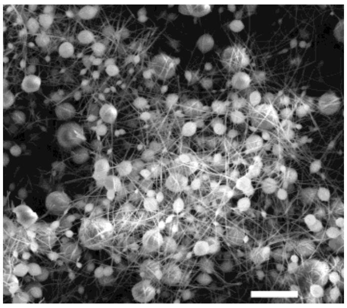

Fig. S2. SEM images of electrospun $La_{0.7}Sr_{0.3}MnO_3$ precursor spheres before calcination. Scale bar: 5 µm.

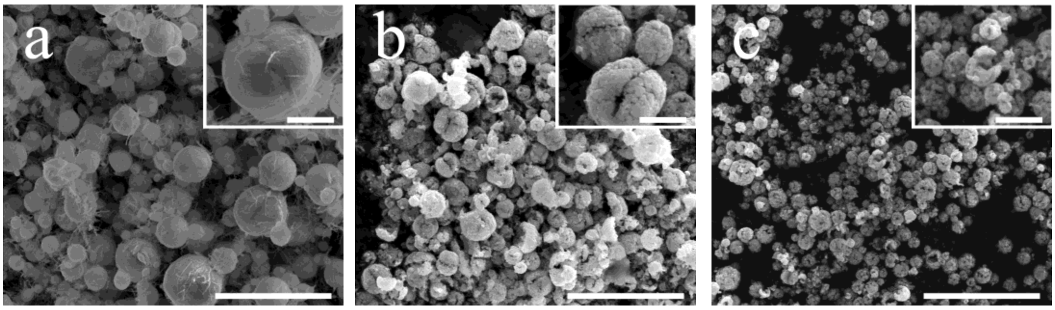

Fig. S3. SEM images of electrospun $La_{0.7}Sr_{0.3}MnO_3$ prepared with the sol containing inorganics amount of (a) 4 mmol, (b) 3 mmol, (c) 2 mmol calcined at 1 °C/min under 650 °C for 5 h. Scale bars: 5 μm and 1 μm for low and high-magnification images, respectively.

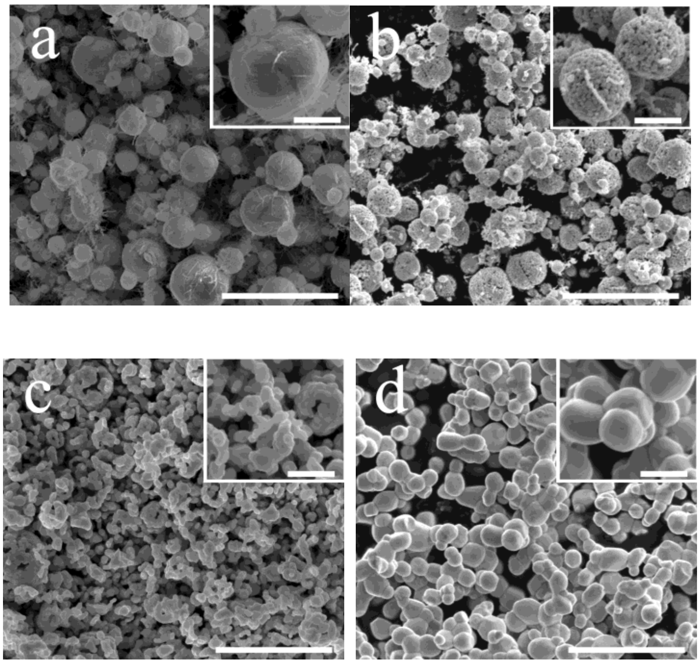

Fig. S4. SEM images of electrospun $La_{0.7}Sr_{0.3}MnO_3$ calcined at the temperature of (a) 650 °C, (b) 750 °C, (c) 950 °C, (d) 1050 °C at 1 °C/min for 5 h. Scale bars: 5 μm and 1 μm for low- and high-magnification images, respectively.

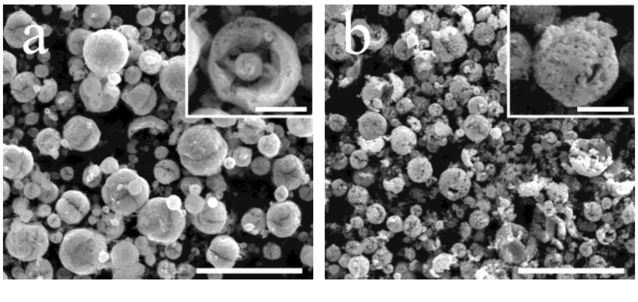

Fig. S5. SEM images showing the evolution process of $La_{0.7}Sr_{0.3}MnO_3$ hollow spheres for different calcination periods: (a) 7 h, (b) 10 h under 650 °C at 1 °C/min. Scale bars: 5 μm and 1 μm for low- and high-magnification images, respectively.

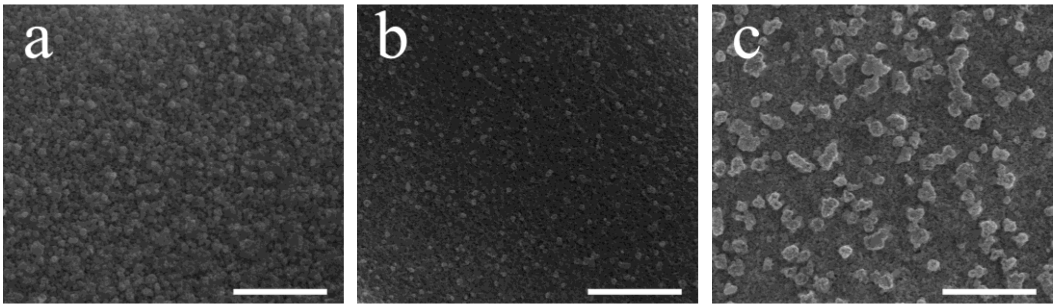

Fig. S6. SEM images of $La_{0.7}Sr_{0.3}MnO_3$ nanoparticles prepared by sol-gel at the heating rate of (a) 1 °C/min, (b) 5 °C/min, (c) 10 °C/min under 650 °C for 5 h. Scale bars: 2 μm.

Table S1. The content of Mn in surface of LSMO and sol-LSMO from quantitative XPS analysis.

Catalyst	Mn (At. %)	Catalyst	Mn (At. %)
LSMO-1	8.21	sol-LSMO-1	7.85
LSMO-5	9.59	sol-LSMO-5	5.53
LSMO-10	5.84	sol-LSMO-10	7.22

Table S2. The BET surface area of LSMO and sol-LSMO determined by nitrogen adsorption/desorption measurements.

Catalyst	S_{BET} (m^2/g)	Catalyst	S_{BET} (m^2/g)
LSMO-1	11.1644	sol-LSMO-1	16.9738
LSMO-5	17.9907	sol-LSMO-5	20.1589
LSMO-10	2.6421	sol-LSMO-10	19.1365

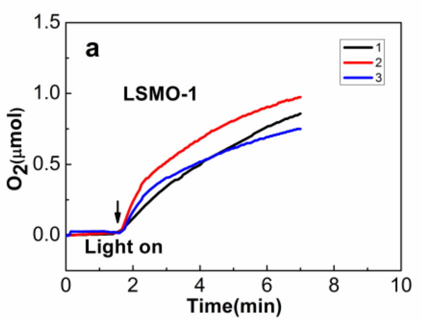

Fig. S7. Time courses of O_2 evolution under visible light irradiation (a Newport oriel sol3A solar simulator through a transmitting glass filter, λ> 420 nm) of a bicarbonate buffer solution (1 mM, 20 mL, pH 7.0) containing $[Ru(bpy)_3]^{2+}$ (0.5 mM), $Na_2S_2O_8$ (10 mM) with 250 ppm catalyst at room temperature in three repetitive examinations.

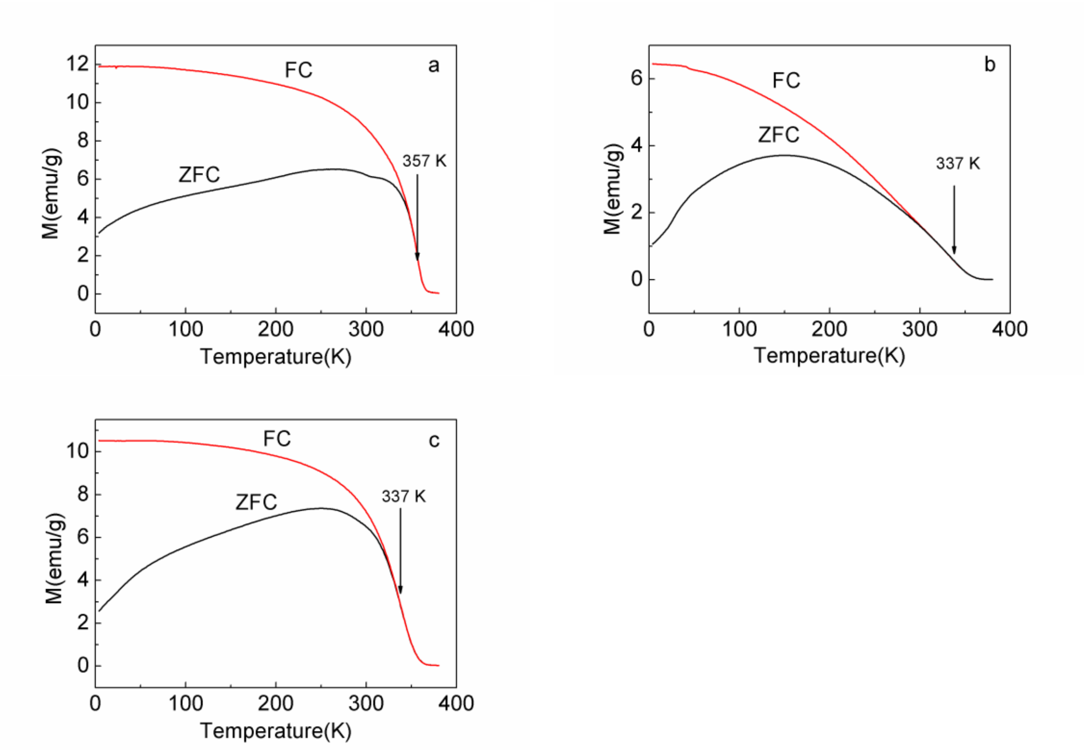

Fig. S8. ZFC and FC magnetization plots (from 4 to 380 K under a 0.1 T field) of $La_{0.7}Sr_{0.3}MnO_3$ hollow spheres calcined at (a) 1 ^{o}C/min, (b) 5 ^{o}C/min, (c) 10 ^{o}C/min under 650 ^{o}C for 5 h.

Table S3. The coercive field, remanent magnetization and saturated magnetization values of (a) LSMO-1, (b) LSMO-5 and (c) LSMO-10.

	M_S(emu/g)	M_R(emu/g)	H_C(Oe)
a (LSMO-1)	74.0	12.1	170.0
b (LSMO-5)	32.3	10.1	368.7
c (LSMO-10)	67.6	13.4	216.6