Electronic Supplementary Information

Synthesis of Low Dimensional Hierarchical Transition Metal Oxides via a Direct Deep Eutectic Solvent Calcining Method for Enhanced Oxygen Evolution Catalysis

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Experimental section

Reagents

D-Glucose monohydrate ($C_6H_{12}O_6{\cdot}H_2O$), urea, ethylenediaminetetraacetic acid (EDTA), citric acid (CA) were purchased from Beijing Chemical Works. $Co(NO_3)_2{\cdot}6H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, $Fe(NO_3)_2{\cdot}9H_2O$ were acquired from Xilong Scientific Co., Ltd. $Ba(NO_3)_2$, $La(NO_3)_3{\cdot}6H_2O$, $Sr(NO_3)_2$, $RuCl_3{\cdot}xH_2O$ were received from Shanghai Aladdin Biochemical Technology Co., Ltd. All of the chemicals are analytical grade without further purification.

Apparatus

Thermal gravimetric analysis (TGA) patterns were collected on Pyris Diamond TGA/DTA (PerkinElmer, U.S.). X-ray powder diffraction (XRD) patterns were recorded on a D8 Advance (Bruker, Germany) diffractometer using Cu-Kα radiation with a Ni filter (λ = 0.154059 nm at 30 kV and 15 mA). Raman spectroscopies were conducted on Renishaw 2000 model confocal microscopy Raman spectrometer with a CCD detector and a holographic notch filter (Renishaw Ltd., Gloucestershire, U.K.). X-ray photoelectron spectroscopy (XPS) measurements were conducted on an ESCALAB-MKII spectrometer (VG Co., United Kingdom) with Al Kα X-ray radiation as the X-ray source for excitation. Scanning electron microscopy (SEM) images were collected on an S-4800 field emission scanning electron microanalyzer (Hitachi, Japan). Transmission electron microscope (TEM) images were obtained on Hitachi H-8100 EM TEM with an accelerating voltage of 100 kV. N_2 adsorption-desorption isotherms were obtained at -196 °C on a NOVA 4200e. Samples were degassed at 100 °C for a minimum of 8 h prior to analysis. Electrochemical experiments were performed using a CHI832C electrochemical workstation (CH Instruments, Shanghai). Rotating ring-disk electrode (RRDE) measurements were performed on a Model RRDE-3A Apparatus (ALS, Japan) with a CHI832C electrochemical workstation.

Experimental

Table S1. Synthetic details of porous metal oxides with DES calcining method

2D porous metal oxides	Amount of DES	Amount of metal precursor salts	With N_2 protection	In the air
$LSCF_{20}$-DES	5 g glucose-urea DES (about 5 mL)	0.1 mmol $La(NO_3)_2 \cdot 6H_2O$, 0.1 mmol $Sr(NO_3)_2$, 0.16 mmol $Co(NO_3)_2 \cdot 6H_2O$, 0.04 mmol $Fe(NO_3)_2 \cdot 9H_2O$	600 °C for 2 h at 10 °C/min	900 °C for 6 h
$BSCF_5$-DES		0.025 mmol $Ba(NO_3)_2$, 0.025 mmol $Sr(NO_3)_2$, 0.04 mmol $Co(NO_3)_2 \cdot 6H_2O$, 0.01 mmol $Fe(NO_3)_2 \cdot 9H_2O$, 0.1 mmol EDTA[a]		
Co_3O_4-DES		0.15 mmol $Co(NO_3)_2 \cdot 6H_2O$		600 °C for 6 h
$NiCo_2O_4$-DES		0.05 mmol $Ni(NO_3)_2 \cdot 6H_2O$, 0.1 mmol $Co(NO_3)_2 \cdot 6H_2O$		
RuO_2-DES		0.1 mmol $RuCl_3 \cdot xH_2O$[b]		

[a]: $Ba(NO_3)_2$ is hardly dissolved into glucose-urea DES. Dissolving $Ba(NO_3)_2$ process refers to Yang's work[1]. Firstly, EDTA was added to the mixture of metal salts and 1 mL DI water. Some precipitation may occur after the addition. Next, concentrated ammonia solution was added drop by drop and stirred until all precipitants were dissolved. Finally, the solution was mixed with glucose-urea DES to form a clear liquid.

[b]: $RuCl_3 \cdot xH_2O$ is also difficult dissolved in the glucose-urea DES. $RuCl_3 \cdot xH_2O$ is dissolved in the 1 mL DI water first, which mixed with glucose-urea DES to form a clear liquid.

Other methods to synthesize metal oxides

$LSCF_{20}$-CA and $BSCF_{20}$-CA were synthesized by the typical citric acid combustion methods.[1] For $LSCF_{20}$-CA, 0.1 mmol $La(NO_3)_2·6H_2O$, 0.1 mmol $Sr(NO_3)_2$, 0.16 mmol $Co(NO_3)_2·6H_2O$, 0.04 mmol $Fe(NO_3)_2·9H_2O$, and 0.4 mmol citric acid were dissolved into 5 mL DI water. Then, the water was removed at 120 °C for 12 h to form a gel and then was heated at 900 °C for 4 h in air with a heating rate of 10 °C/min. For $BSCF_{20}$-CA, 0.1 mmol $Ba(NO_3)_2$, 0.1 mmol $Sr(NO_3)_2$, 0.16 mmol $Co(NO_3)_2·6H_2O$, 0.04 mmol $Fe(NO_3)_2·9H_2O$, 0.4 mmol citric acid and 0.4 mmol EDTA were added to 5 mL DI water, and concentrated ammonia solution was added into the solution drop by drop until all precipitations dissolved thoroughly. The solution was heated at 120 °C to remove water and form a gel. Then, the gel was calcined at 900 °C for 4 h in air with a heating rate of 10 °C/min.

Co_3O_4 and $NiCo_2O_4$ were synthesized according to modified Sun's work.[2] For Co_3O_4, 1.5 g $Co(NO_3)_2·6H_2O$ was heated at 900 °C for 4 h in the air and then cooled to room temperature. For $NiCo_2O_4$, the metal salt precursors were changed to 0.5 g $Co(NO_3)_2·6H_2O$, 1.0 g $Ni(NO_3)_2·6H_2O$ and dissolving into 5 mL H_2O. Then the solution heated at 120 °C to remove water to acquire salt mixture. Then the mixture was heated at 900 °C for 4 h in the air.

RuO_2 was synthesized by wet-chemical method according to Cheng's work.[3] An aqueous solution containing 0.01 mol of $RuCl_3·xH_2O$ was heated (100 °C) with magnetic stirring for 10 min, and 1 mL of NaOH (1 mol/L) was added to the solution to obtain the precursor Ru-hydroxide. The obtained mixture was continuously heated at 100 °C for 45 min under stirring, and then the precipitate was washed several times and calcined at 350 °C for 1 h to obtain the RuO_2.

Electrochemical measurements

All the electrochemical measurements were carried out at room temperature. The electrochemical measurement of OER was performed by using a Model RRDE-3A Apparatus (BAS, Japan) with a CHI832c electrochemical workstation. An RDE was used as working electrode for the test of OER activity. A KCl saturated Ag/AgCl electrode was used as the reference electrode and was calibrated with respect to RHE ($E_{RHE} = E_{Ag/AgCl} + 0.059\ pH + 0.197$) and Pt wire was used as counter electrodes.

Before modification, RDE was polished with alumina slurry. Then, it was washed successively with an alcohol/water (1:1) mixture in an ultrasonic bath and dried in the air. To remove any electrode conductivity limitations, all the catalysts were mixed with conductive carbon black (VK72-1R) as a mass ratio of 2:1. Briefly, the electrocatalyst suspensions were prepared by sonication of a mixture of oxide and conductive carbon black (1 mg), Nafion solution (5 wt%, 10 μL) and ethanol (200 μL) for 1 h to generate a homogeneous ink. Next 10 μL aliquot of as-prepared catalyst ink was dropped on the surface of the RDE, yielding an approximate catalyst of 0.398 mg_{cat}/cm^2 and left to dry in the air for the OER tests.

In RDE measurements, linear sweep voltammetry (LSV) was conducted in an oxygen-saturated KOH solution (pH 14) at room temperature using a scan rate of 5 mV/s and a rotation speed of 1600 rpm. All LSV polarization curves were corrected with 95% IR-compensation.

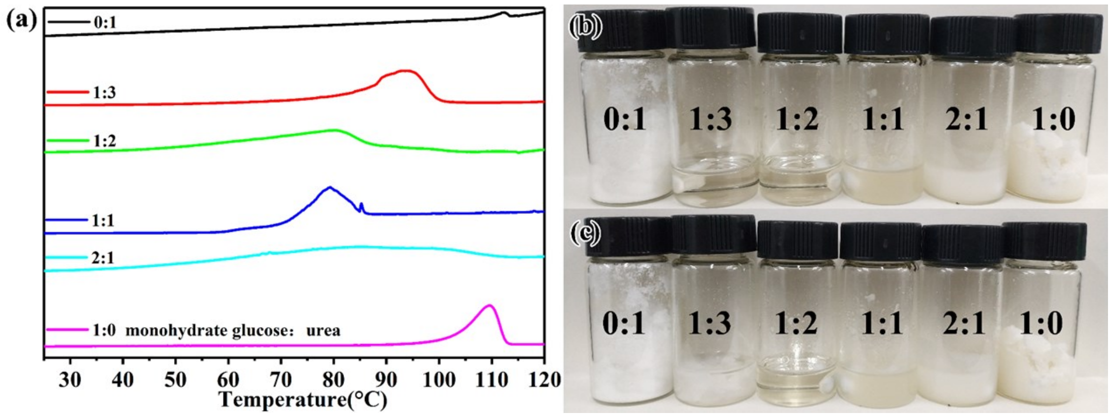


Fig. S1. (a) The DSC curves of glucose-urea mixtures with different monohydrate glucose : urea molar ratio. The photos of glucose-urea mixtures with different monohydrate glucose : urea molar ratios after heating for 1 h at 80 °C (b) and cooled at room temperature for 30 min (c).

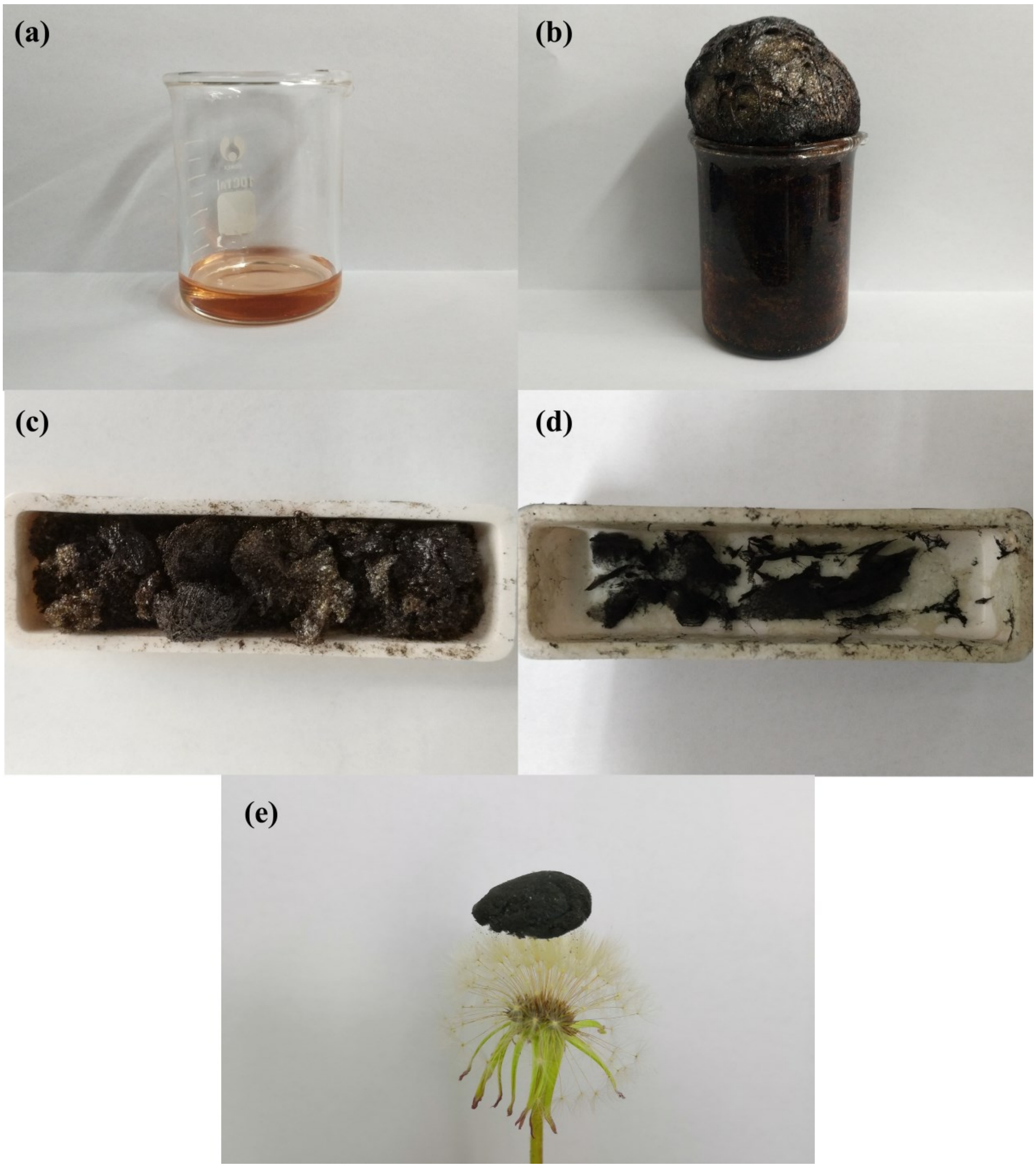
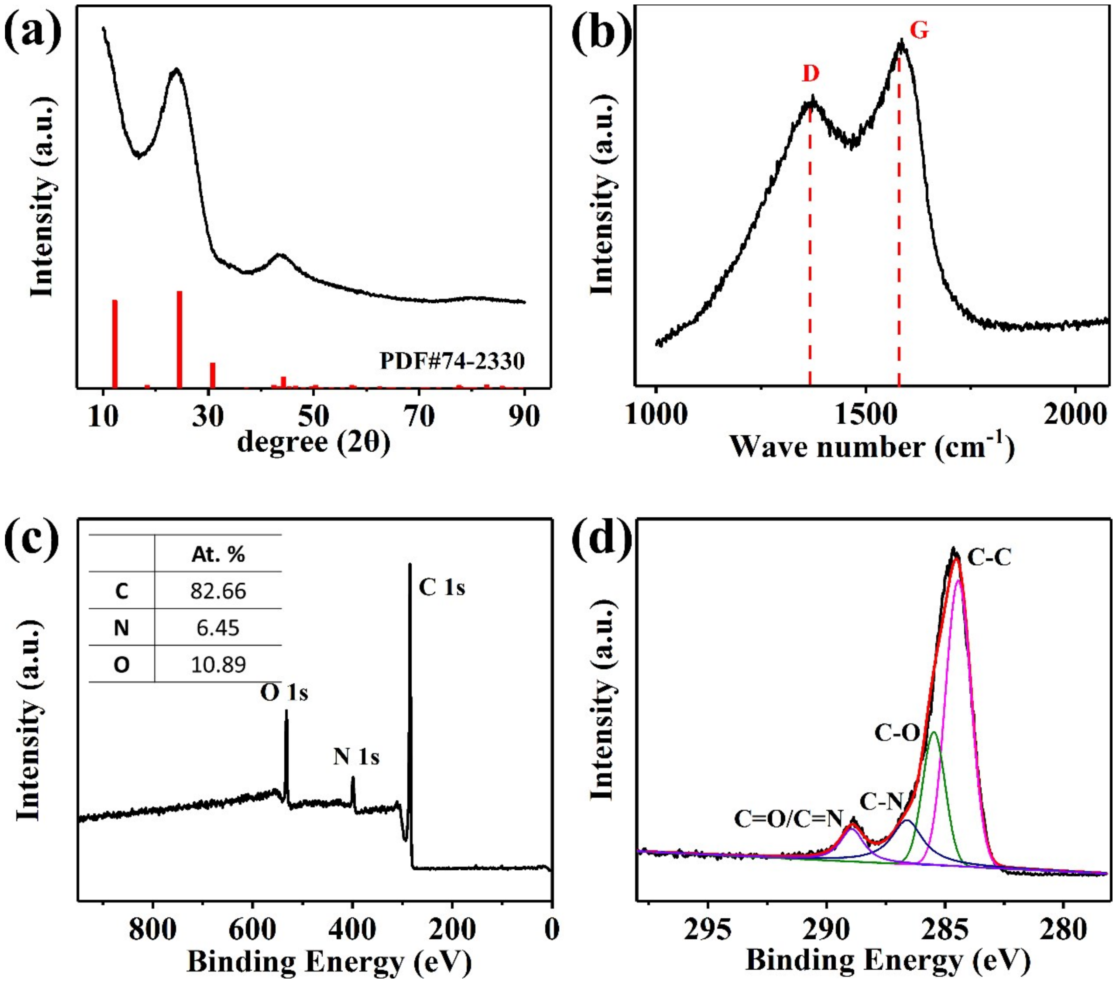


Fig. S2. The photos of (a) glucose-urea DES containing LSCF metal precursors (b) black foam made after microwave heating; (c) the foam transferred to the porcelain boat; (d) the 2D porous LSCF made by DES calcining method; and (e) the 2D porous LSCF on the dandelion.



	At. %
C	82.66
N	6.45
O	10.89

Fig. S3. (a) XRD patterns of the carbon templates made by calcining glucose-urea DES in N_2 atmosphere. (b) Raman spectrum of the carbon templates; (c) XPS overall spectrum of the carbon templates. The inset shows content of C, N, and O on XPS analysis. (d) C 1s spectrum of carbon templates.

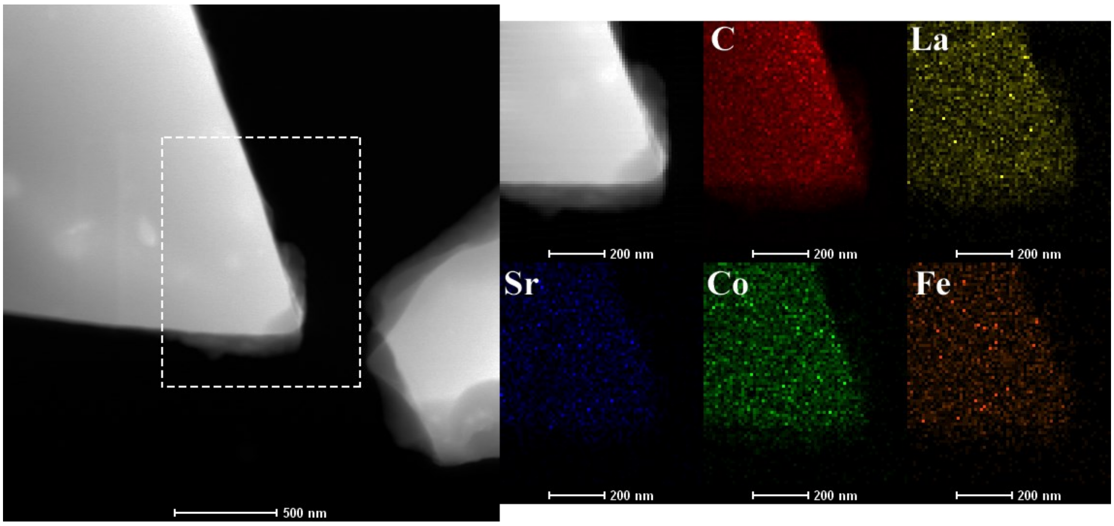


Fig. S4. TEM image of LSCF (left) and STEM-EDS mappings (right) of carbon flake templates with LSCF metal precursors.

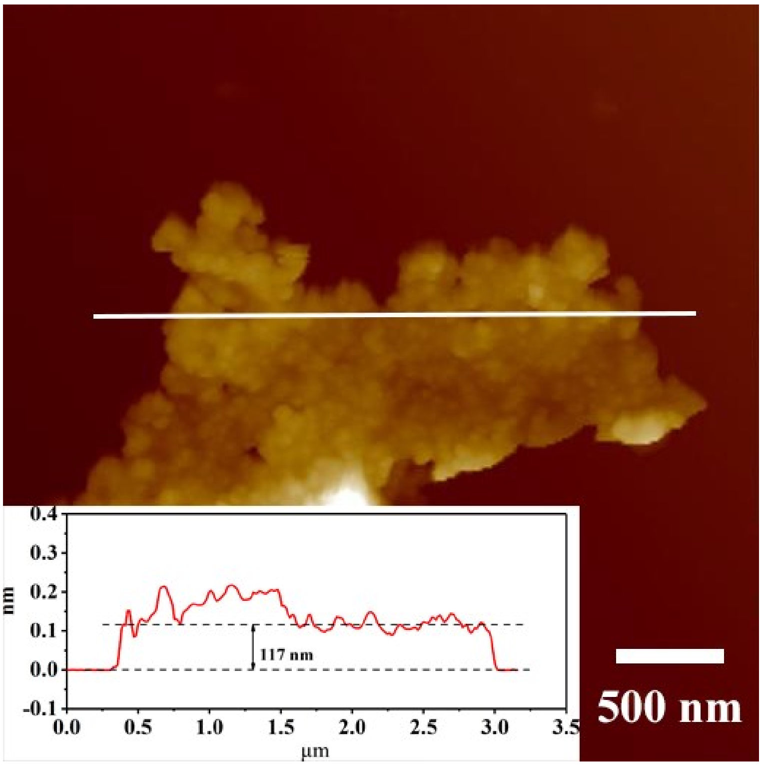


Fig. S5. AFM image of $LSCF_{20}$-DES.

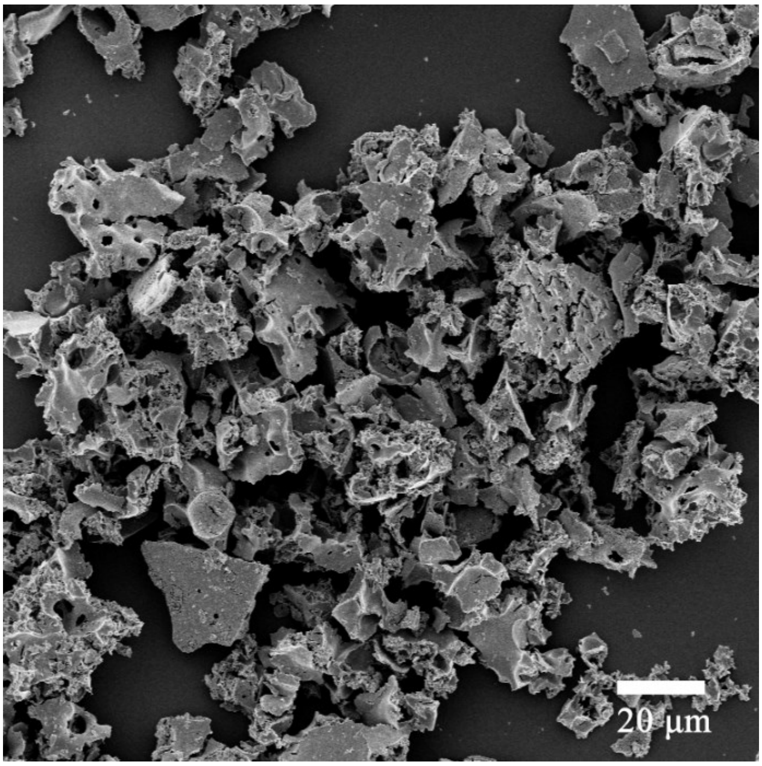


Fig. S6. SEM image of $LSCF_{20}$-CA.

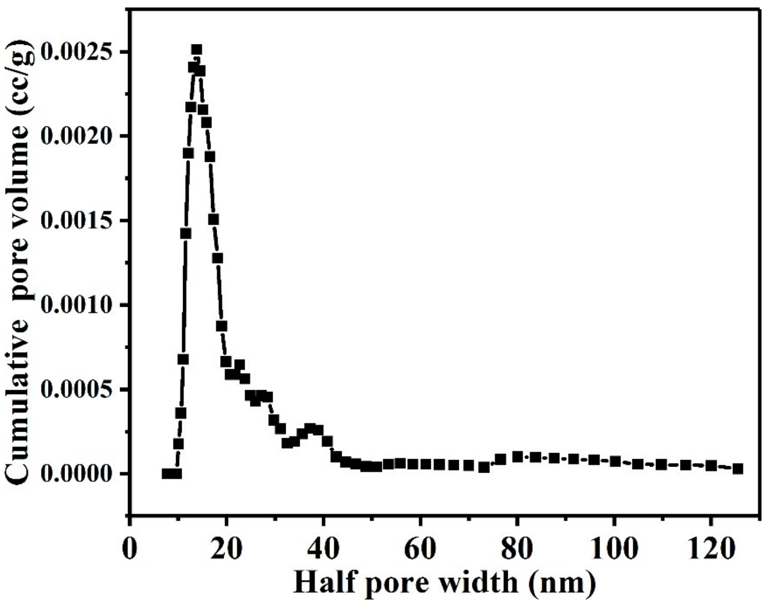


Fig. S7. Pore size distribution of $LSCF_{20}$-DES

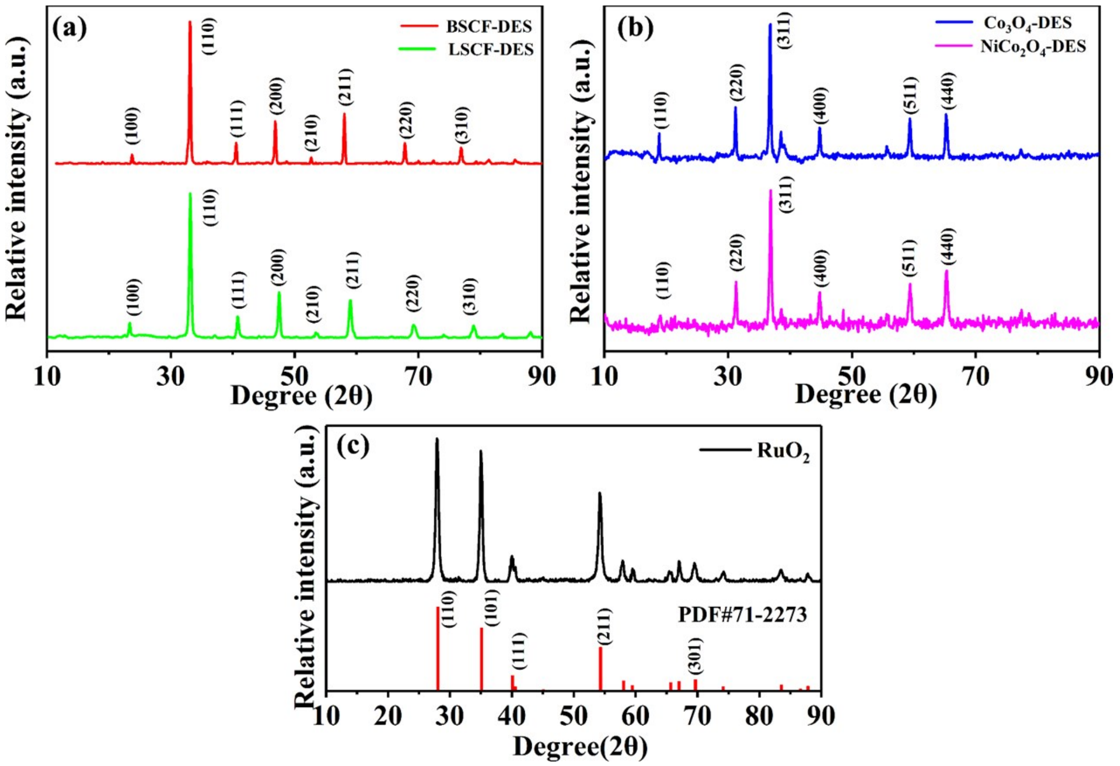


Fig. S8. XRD patterns of porous $La_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$, $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$, Co_3O_4, $NiCo_2O_4$ and RuO_2 synthesized by DES calcining method.

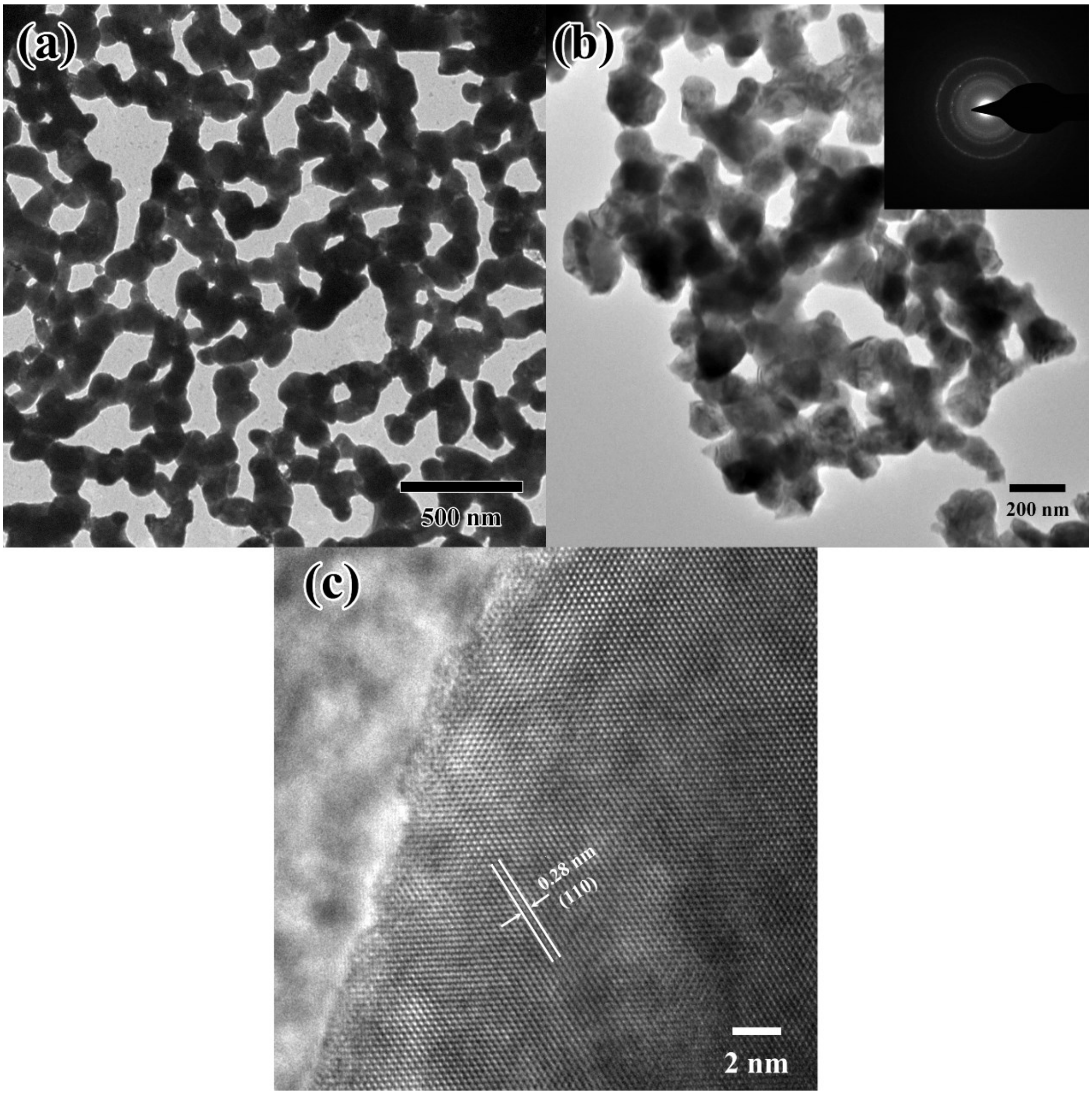


Fig. S9. (a, b) TEM image, (c) HRTEM image of LSCF$_{20}$-DES. The inset of Fig. S9b shows SAED of LSCF$_{20}$-DES.

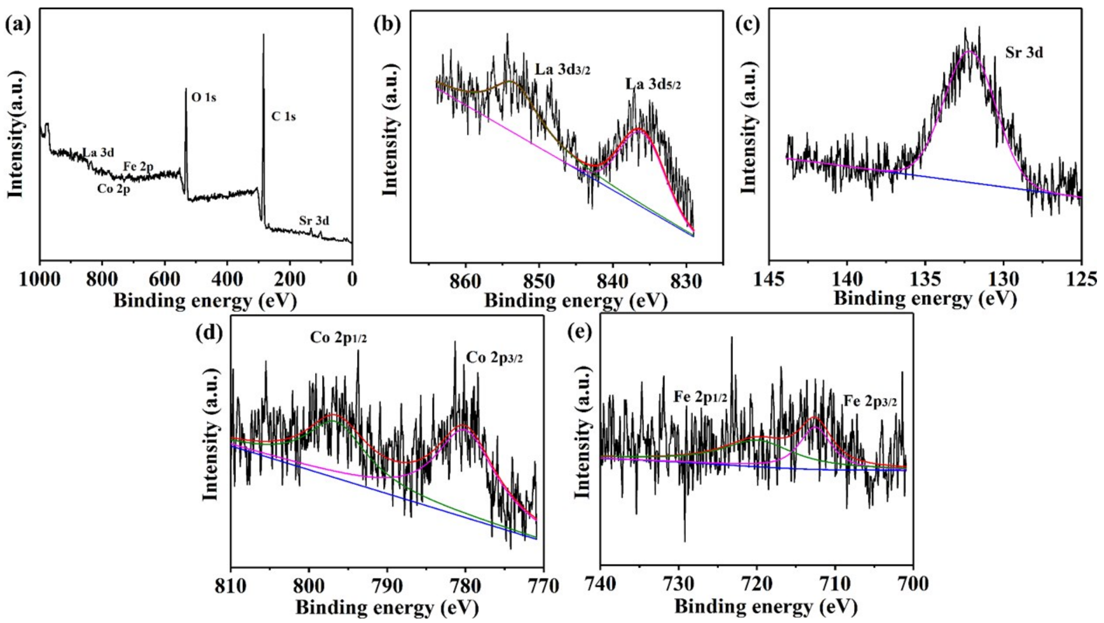


Fig. S10. (a) XPS survey spectrum of LSCF$_{20}$-DES, (b-e) La 3d, Sr 3d, Co 2p, Fe 2p spectra of LSCF$_{20}$-DES.

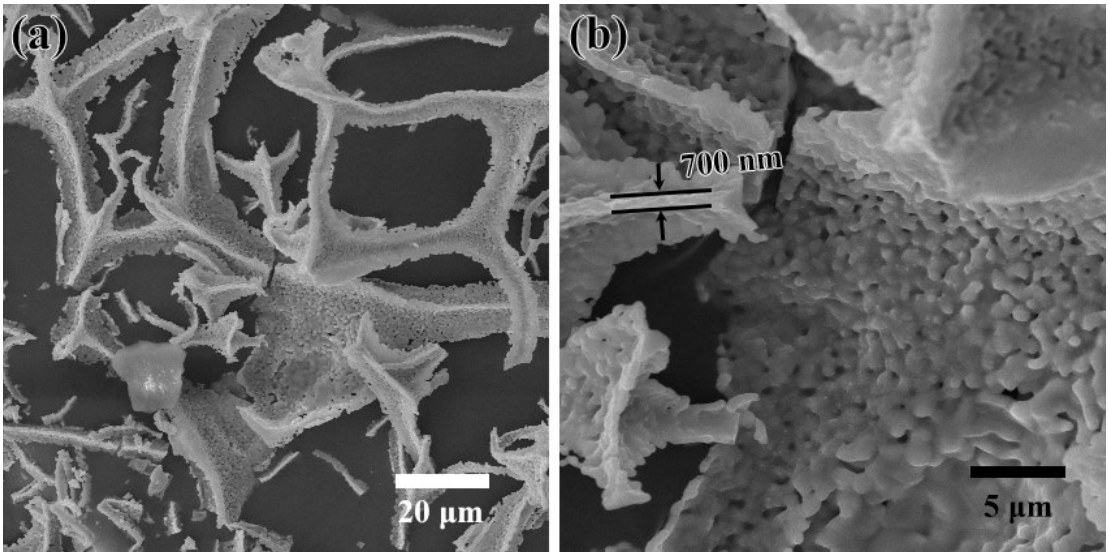


Fig. S11. (a, b) SEM images of LSCF_{10}-DES. The width of the ridge is about 700 nm.

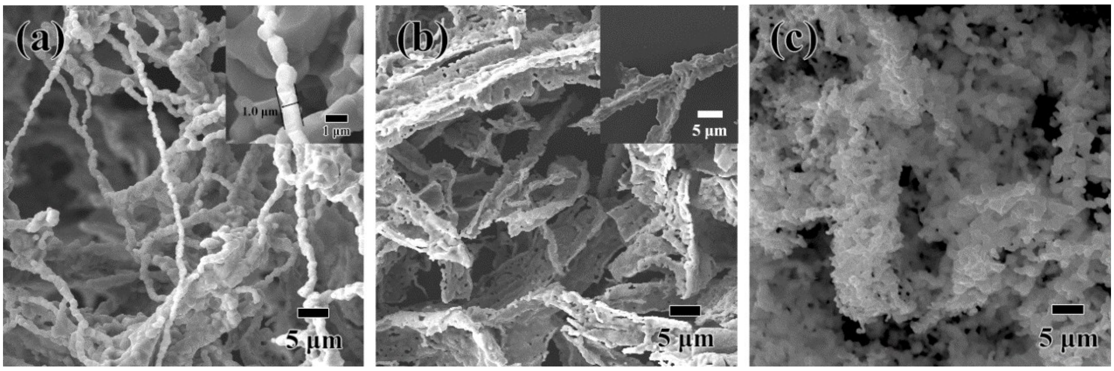


Fig. S12. SEM images of (a) $BSCF_{10}$-DES, (b) $BSCF_{50}$-DES and (c) $BSCF_{100}$-DES.

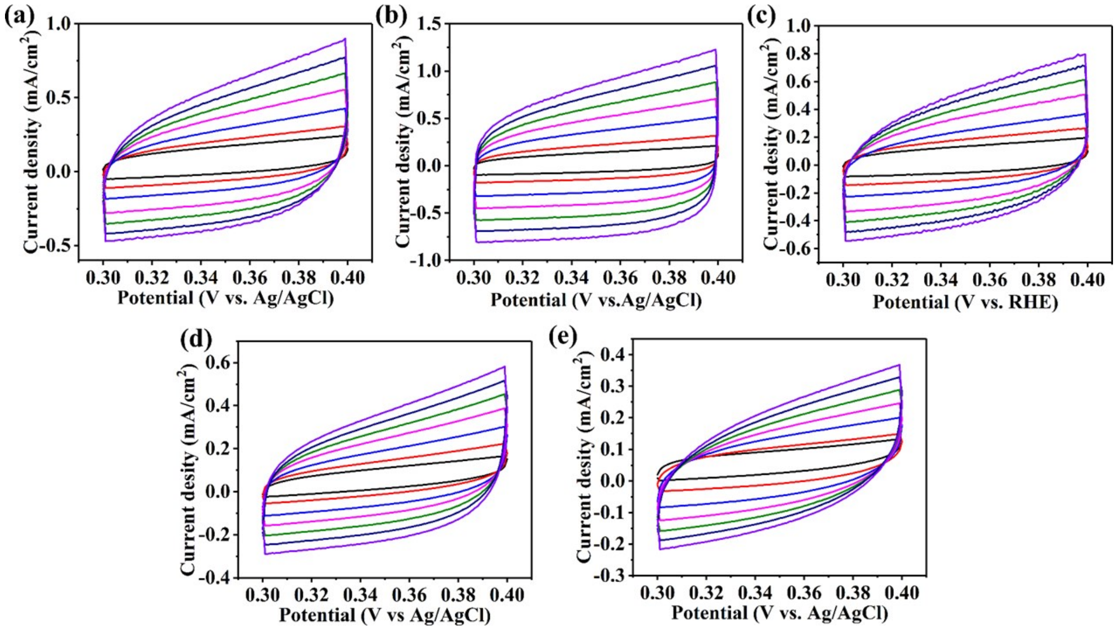


Fig. S13. CVs of (a) LSCF$_{10}$-DES, (b) LSCF$_{20}$-DES, (c) LSCF$_{50}$-DES, (d) LSCF$_{100}$-DES and (e) LSCF$_{20}$-CA at different scan rates (10, 20, 40, 60, 80, 100 and 120 mV/s).

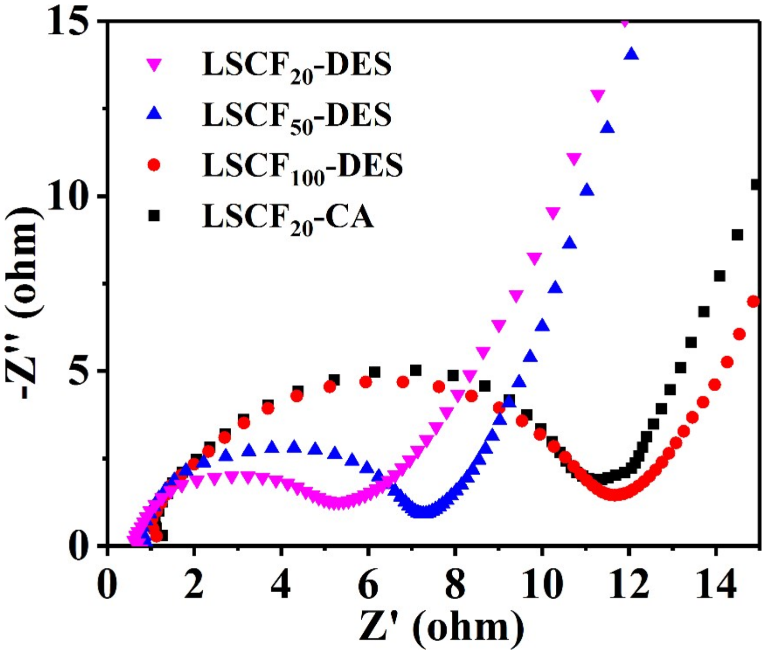


Fig. S14. Electrochemical impedance spectra of LSCFs catalysts recorded at 1.573 V (vs. RHE).

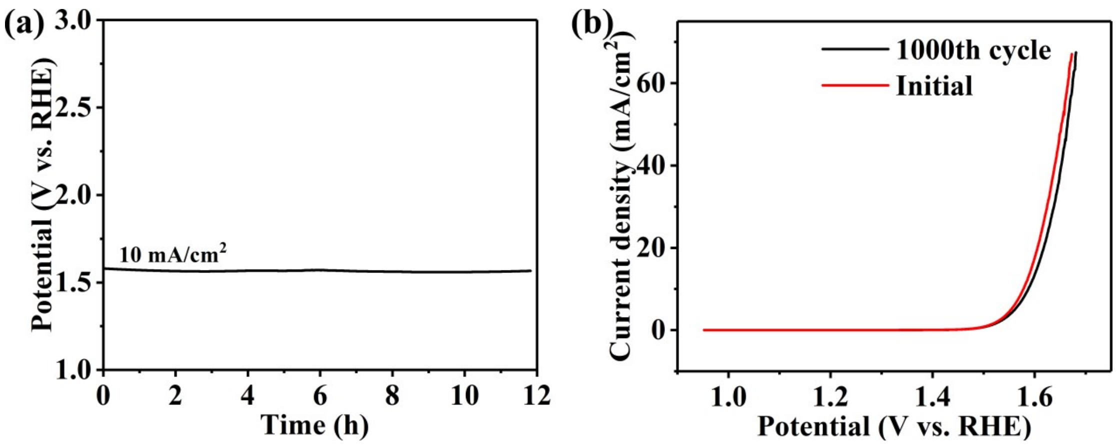


Fig. S15. (a) The potential-time curve of $LSCF_{20}$-DES measured at the current density of 10 mA/cm^2. (b) Polarization curves of $LSCF_{20}$-DES before and after 1000 cycles at a scan rate of 100 mV/s between 0.95~1.65 V (vs. RHE)

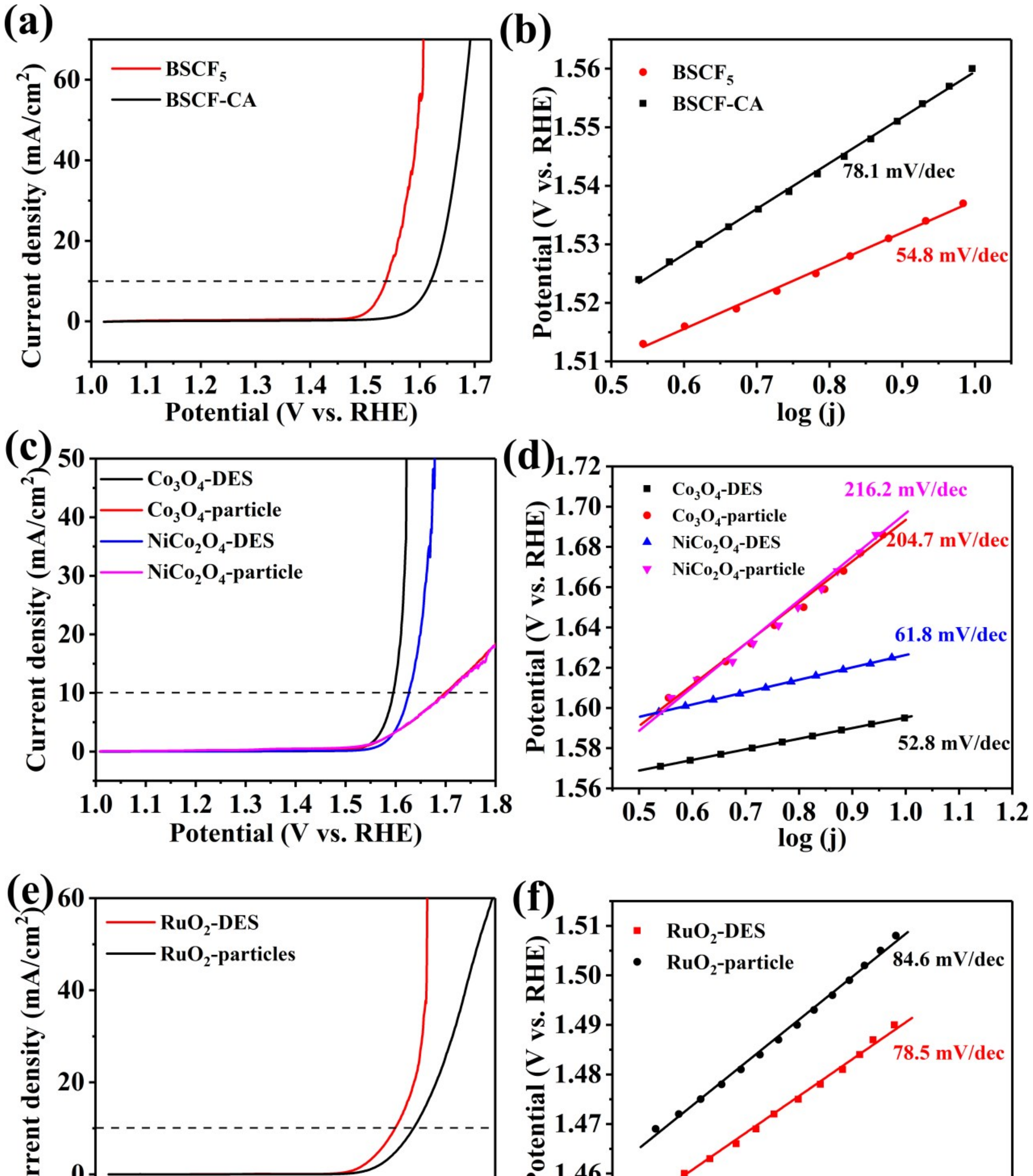


Fig. S16. The comparison of LSV curves and Tafel plots between TMOs synthesized by DES calcining method and other classical methods (Citric acid combustion method for LSCF, BSCF and wet chemical method for Co_3O_4, $NiCo_2O_4$ and RuO_2).

Table S2. OER electrolytic activities of TMOs synthesized by DES calcining method and OER catalytic activities of other perovskite oxides reported previously.

TMO catalysts	Electrolyte	Overpotential at 10 mV/cm^2	Tafel plots (mV/dec)	Reference
$LSCF_{20}$-DES	1.0 M KOH	0.304 V	62.9	This work
$BSCF_5$-DES	1.0 M KOH	0.315 V	54.8	This work
Co_3O_4-DES	1.0 M KOH	0.365 V	52.8	This work
$NiCo_2O_4$-DES	1.0 M KOH	0.397 V	61.8	This work
RuO_2-DES	1.0 M KOH	0.297 V	78.5	This work
$La_{0.3}(Ba_{0.5}Sr_{0.5})_{0.7}Co_{0.8}Fe_{0.2}O_{3-\delta}$	0.1 M KOH	0.33 V (evaluated from LSV curves)	——	[4]
$SrNb_{0.1}Co_{0.7}Fe_{0.2}O_{3-\delta}$	0.1 M KOH	0.42 V	90	[5]
$SrCo_{0.95}P_{0.05}O_{3-\delta}$	0.1 M KOH	0.48 V	84	[6]
$Ca_{0.9}Yb_{0.1}MnO_3$	0.1 M KOH	0.50 V	68	[7]
$BaCo_{0.7}Fe_{0.2}Sn_{0.1}O_{3-\delta}$	0.1 M KOH	0.45 V	63	[8]
phosphorus-doped $LaFeO_{3-\delta}$	0.1 M KOH	0.46 V	50	[9]
$(La_{0.8}Sr_{0.2})_{1+x}MnO_3$	0.1 M KOH	0.57 V	109	[10]
$Ca_{2-x}Sr_xFe_2O_{6-\delta}$	0.1 M KOH	0.42 V	60	[11]
$LaFe_xNi_{1-x}O_3$ nanorods	1.0M KOH	0.319 V	50	[12]

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