

Supplementary Information

Metal Oxide Electrocatalyst Support for Carbon-free Durable Electrodes with Excellent Corrosion Resistance at High Potential Conditions

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Experimental Procedures

Chemicals

ENETIA[®] Ti₂O₃ was kindly provided by Sakai Chemical Industry Co., Ltd. (Sakai, Japan), and its crystal structure was confirmed by X-ray diffraction (XRD) measurement (Fig. S1). Barium acetate (Ba(OAc)₂, 99%), cobalt (II) acetate tetrahydrate (Co(OAc)₂·4H₂O, 99%), strontium acetate 0.5-water (Sr(OAc)₂·0.5H₂O, 99%), and L-aspartic acid (99%) were purchased from Kanto Chemical Co., Inc. (Tokyo, Japan). Potassium hydroxide (KOH, 85%) was purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Multiwall carbon nanotubes (MWCNTs) (90%) with an average diameter of 9.5 nm were purchased from Nanocyl SA. (Sambreville, Belgium) and functionalized for hydrophilization as reported in our previous paper.¹ Iron (II) acetate (Fe(OAc)₂, 99.99%) and a 5.0 wt% Nafion[®] solution (product number: 274704) were purchased from Sigma-Aldrich Japan K.K. (Tokyo, Japan). All other chemicals were purchased from Wako Pure Chemical Industries, Ltd. and used as received.

Catalyst synthesis

Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} (BSCF) was synthesized *via* the aspartic acid-aided sol-gel method.² Ba(OAc)₂ (2.55 g, 10.0 mmol), Sr(OAc)₂·0.5H₂O (2.15 g, 10.0 mmol), Co(OAc)₂·4H₂O (3.99 g, 16.0 mmol), Fe(OAc)₂ (0.697 g, 4.00 mmol), and L-aspartic acid (7.99 g, 60.0 mmol) were placed into a 300 mL round-bottom flask. Then, 100 mL of deionized water was added into the flask. The mixture was heated to 70 °C with rotation at 100 rpm to dissolve the solids; subsequently, the water was evaporated in vacuo at 70 °C. The residual solid was ground in a mortar and dried in air at 230 °C. The residual solid was ground again and then calcined in air at 950 °C for 5 h to yield BSCF as a black powder.

A series of BSCF/Ti₂O₃ was fabricated by annealing BSCF with Ti₂O₃ in an inert atmosphere. BSCF and Ti₂O₃ were mixed and ground in a mortar. The weight composition of BSCF was varied between 10 and 90 wt%. Then, the solid was calcined in a N₂ atmosphere at 200, 400, 600, 800, or 1000 °C for 4 h to yield 10–90BSCF/Ti₂O₃_200, 400, 600, 800, or 1000.

Structural characterizations

XRD measurements were conducted using a diffractometer (MiniFlex 600, Rigaku Corporation, Akishima, Japan; Cu K α radiation, $\lambda = 1.5405$ Å, 40 kV, 15 mA) equipped with a high-speed one-dimensional detector (D/teX Ultra, Rigaku Corporation). Diffraction data were recorded in the range of $2\theta = 10$ – 90° at 0.02° steps and a scan rate of $20^\circ \text{ min}^{-1}$.

Raman spectra were obtained on a confocal laser Raman microscope (LabRam HR Evolution, HORIBA, Ltd., Kyoto, Japan) with a laser wavelength of 532 nm. Spectra were recorded in the range of 200 – 700 cm^{-1} using a grating of 1800 gr/min, and the measurements were conducted at room temperature.

Ultraviolet-visible (UV-vis) diffuse reflectance spectra were obtained on a UV-vis spectrophotometer (UV-2600, Shimadzu Corporation, Kyoto, Japan).

Scanning electron microscopy (SEM) images were recorded with a Hitachi S-5500 (Hitachi High-Technologies Corporation, Tokyo, Japan) at an accelerating voltage of 5.0 kV.

Transmission electron microscopy (TEM) images were recorded with a Hitachi H-9500 (Hitachi High-Technologies Corporation) at an accelerating voltage of 200 kV.

High-resolution (HR-) TEM images were obtained with a JEM-2100F HK (JEOL Ltd., Akishima, Japan) at an accelerating voltage of 200 kV. Before observation, the cross sections of sample particles were created by a focused ion beam process.

High-angle annular dark-field scanning TEM (HAADF-STEM) images were obtained using a JEM-ARM200F (JEOL Ltd.) at an accelerating voltage of 200 kV.

Energy-dispersive X-ray (EDX) spectroscopic elemental mappings on STEM and SEM images were measured using a JED-2300T (JEOL Ltd.) equipped with a silicon drift detector and X-MaxN (Oxford Instruments plc, Abingdon-on-Thames, UK), respectively.

Brunauer–Emmett–Teller (BET) analysis was conducted to quantify specific surface areas using a surface area and pore size analyzer (Nova-4200e, Quantachrome Instruments, Boynton Beach, USA). Nitrogen adsorption/desorption isotherms were obtained at 77 K after the removal of physisorbed water in the particles at 423 K for 1 h under vacuo. The surface areas were calculated over the relative pressure (P/P_0) range of 0.05–0.30.

Electric conductivity measurements were conducted by a two-probe AC impedance method using a Solatron 1260 impedance analyzer (Solatron analytical, Farnborough, UK) in the frequency range of 1 MHz to 100 Hz at an amplitude of 5 mV. The resistance was recorded as the crossing point of the Re Z axis. Sample pellets were prepared by pressing a catalyst powder at 4 ton under vacuum for 10 min. The electric conductivity σ [S cm^{-1}] was calculated using the following equation:

$$R = d/A\sigma$$

where R , d , and A are the resistance [Ω], thickness [cm], and cross-section area [cm^2] of the sample pellets, respectively.

Electrochemical measurements

Electrochemical measurements were conducted on a potentiostat system HZ-7000 (HOKUTO DENKO Corp., Tokyo, Japan) equipped with a rotating disk electrode (RDE) made of a glassy

carbon (geometric area = 0.196 cm²). Fig. S2 shows the setup of the electrochemical measurements. Hg/HgO (1 M KOH) and Pt wire were used as the reference and counter electrodes, respectively. The potential scale was converted from Hg/HgO to the reversible hydrogen electrode (RHE) and expressed in terms of RHE. The calibration of Hg/HgO was performed using the method reported by Li *et al.*³ For calibration, a 1 M KOH solution was saturated with hydrogen by bubbling for 30 min. A Pt disk was used as the working electrode. Hg/HgO and Pt wire were used as reference and counter electrodes, respectively. Linear sweep voltammetry (LSV) was conducted at the scan rate of 1 mV s⁻¹. The potential was recorded where the LSV curve crossed the zero current (= 0.8915 V). The recorded potential was used for calibrating Hg/HgO to RHE using the following equation:

$$E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.8915 \text{ V}$$

Ohmic losses were corrected using the measured current (*i*) and electrolyte resistance (*R*), which was measured by AC impedance at 100 kHz with an amplitude of 5 mV, using the following equation:

$$iR\text{-corrected } E = E_{\text{RHE}} - iR$$

The catalyst slurry of BSCF/Ti₂O₃ was prepared by sonicating a mixture of a certain weight of BSCF/Ti₂O₃, 0.4 mL of a 5.0 wt% Nafion[®] solution, 0.42 mL of isopropanol, and 1.18 mL of deionized water for 2 h in an ice bath. A total of 7 μL of the resulting slurry was dropped onto RDE. The dropped slurry on the electrode was dried by rotation at 600 rpm. The loading amount of BSCF was maintained as 0.178 mg cm⁻²_{disk} on the electrode surface. The electrode sample of 50BSCF/Ti₂O₃_PM was also prepared by the same protocol using a physical mixture of BSCF and Ti₂O₃ without annealing. Additionally, the electrode sample of BSCF/CNT was prepared by the

same protocol using pristine BSCF and functionalized MWCNT as described in our previous report.¹ The sample electrodes were pretreated by ten cyclic voltammetry scans between 0.1 and 1.2 V (RHE) at the scan rate of 50 mV s⁻¹ in a N₂-saturated 1 M KOH solution. Electrolyte solutions were saturated by N₂-saturated bubbling for 30 min before measurements. The oxygen evolution reaction (OER) activities of the oxides were evaluated by reverse scan sweeps between 1.2 and 1.8 V at the scan rate of 10 mV s⁻¹ with an electrode rotation rate of 1600 rpm in O₂-saturated 1 M KOH at room temperature. Electrolyte solutions were saturated by O₂ bubbling for 1 h before measurements. The OER currents were recorded as the average of forward and backward scans of the 10th cycle to cancel the capacitive currents.

Supplementary Figures and Tables

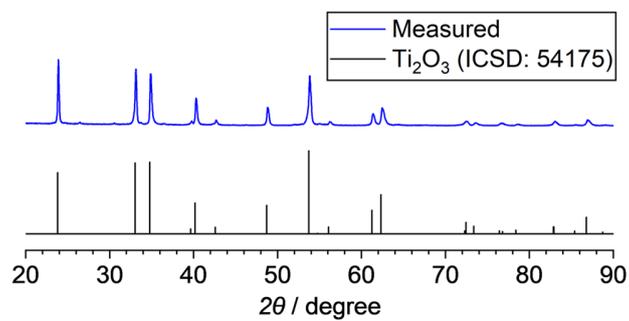


Fig. S1 XRD patterns of (blue) pristine Ti₂O₃ and (black) theoretical Ti₂O₃ (ICSD: 54175).

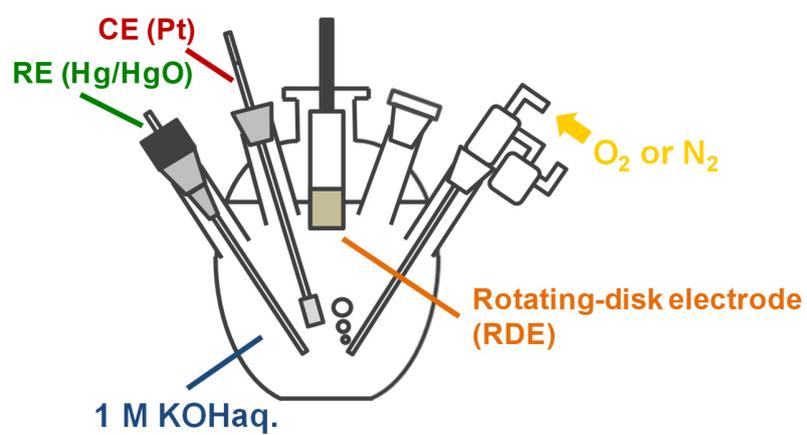


Fig. S2 Set up for the electrochemical measurements in the present study.

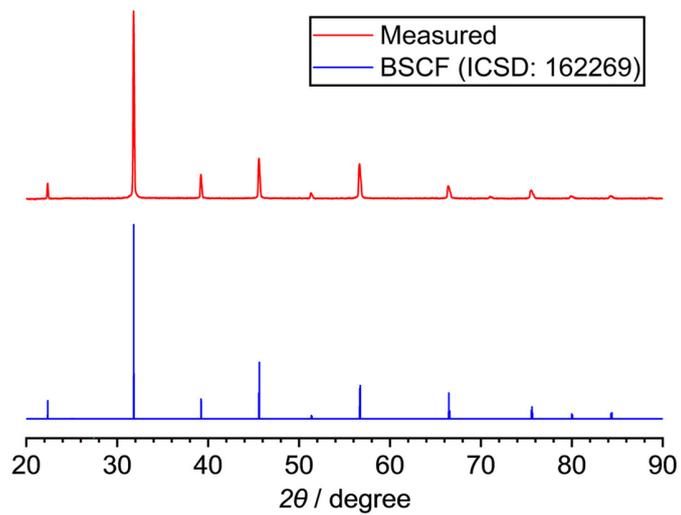


Fig. S3 XRD patterns of (red) synthesized BSCF and (blue) theoretical orthorhombic BSCF (ICSD: 162269).

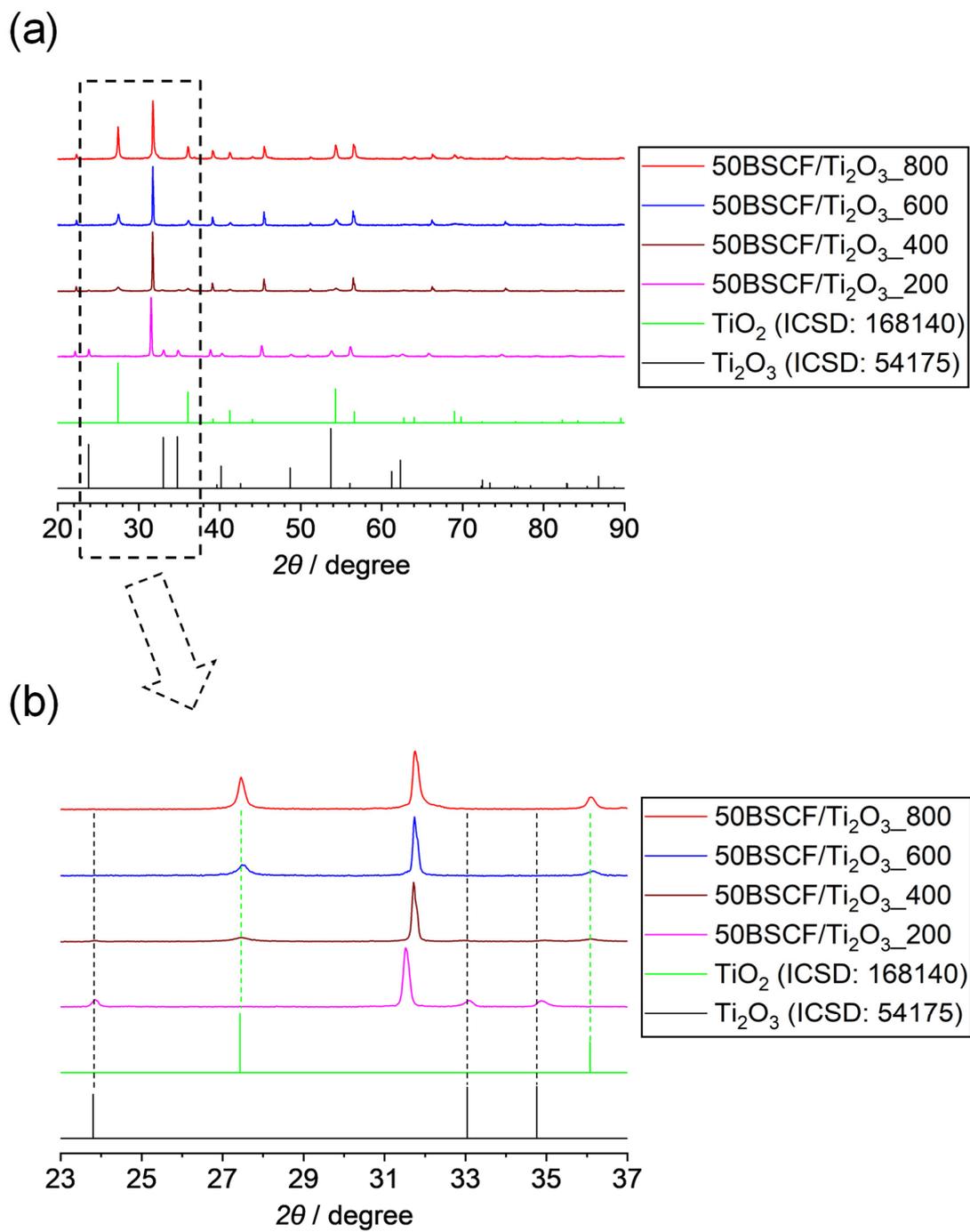


Fig. S4 (a) XRD patterns of 50BSCF/Ti₂O₃_200, 50BSCF/Ti₂O₃_400, 50BSCF/Ti₂O₃_600, and 50BSCF/Ti₂O₃_800 samples. (b) Partial XRD patterns from (a) between two theta values, 23 and 37°.

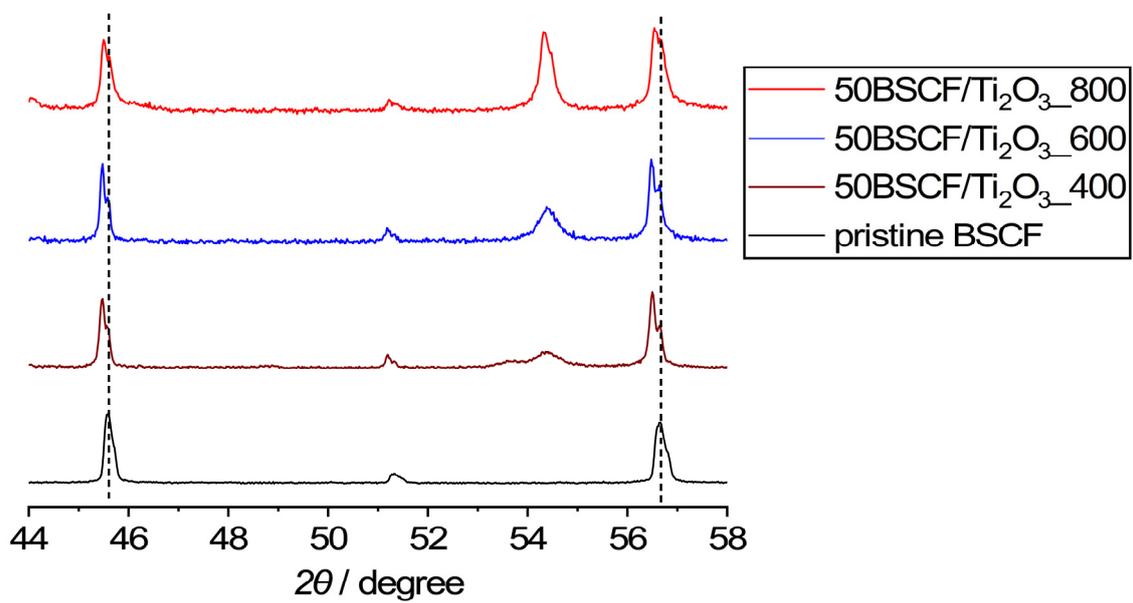


Fig. S5 Partial XRD patterns of 50BSCF/Ti₂O₃_400, 50BSCF/Ti₂O₃_600, and 50BSCF/Ti₂O₃_800, as well as of pristine BSCF between two theta values, 44 and 58°.

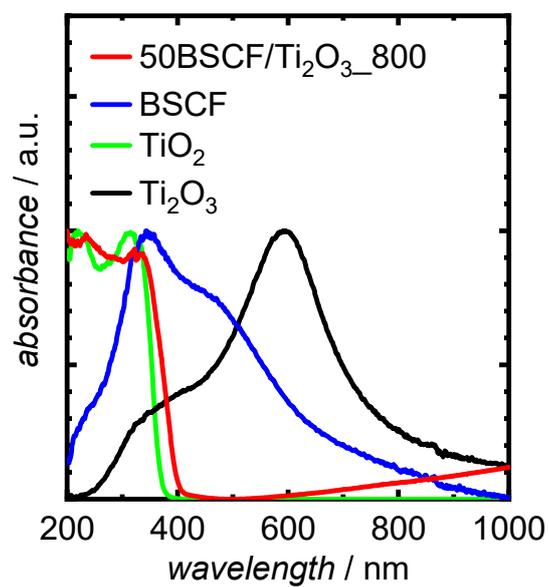


Fig. S6 UV-vis spectra of pristine Ti₂O₃, TiO₂, synthesized BSCF, and 50BSCF/Ti₂O₃_800.

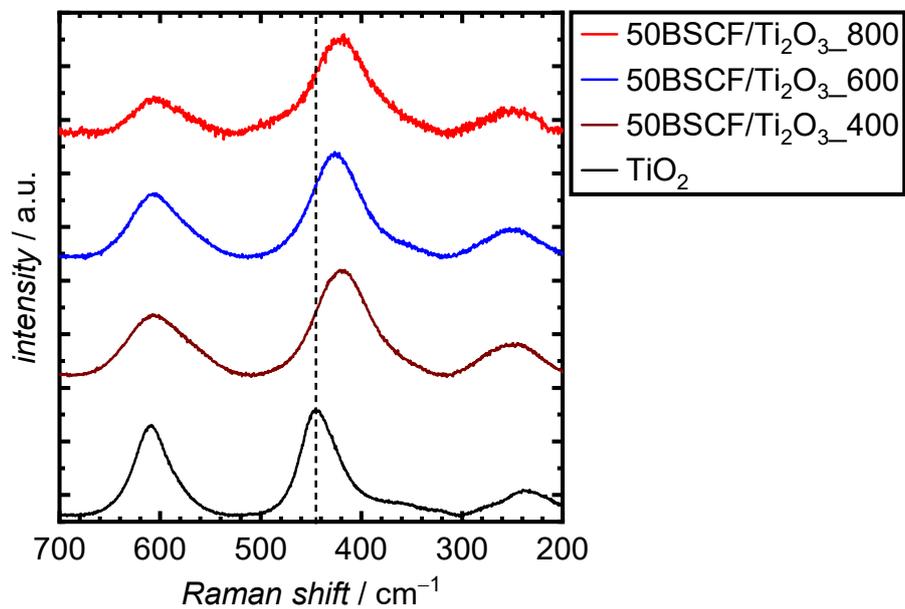


Fig. S7 Raman spectra of 50BSCF/Ti₂O₃_400, 50BSCF/Ti₂O₃_600, and 50BSCF/Ti₂O₃_800 as well as of pristine TiO₂.

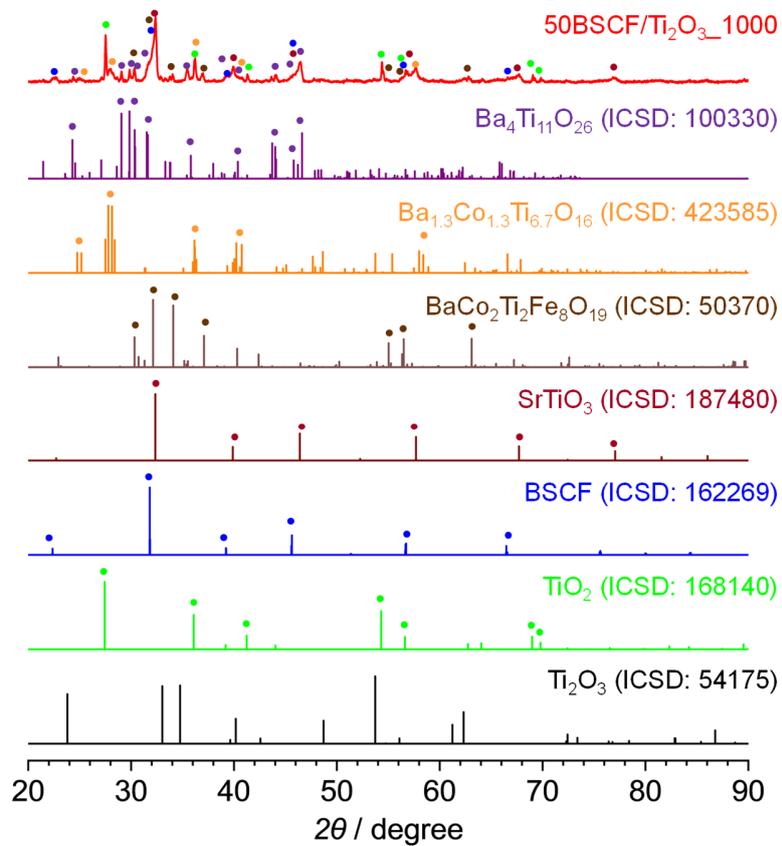


Fig. S8 XRD patterns of 50BSCF/Ti₂O₃_1000 and assignable theoretical compounds from ICSD.

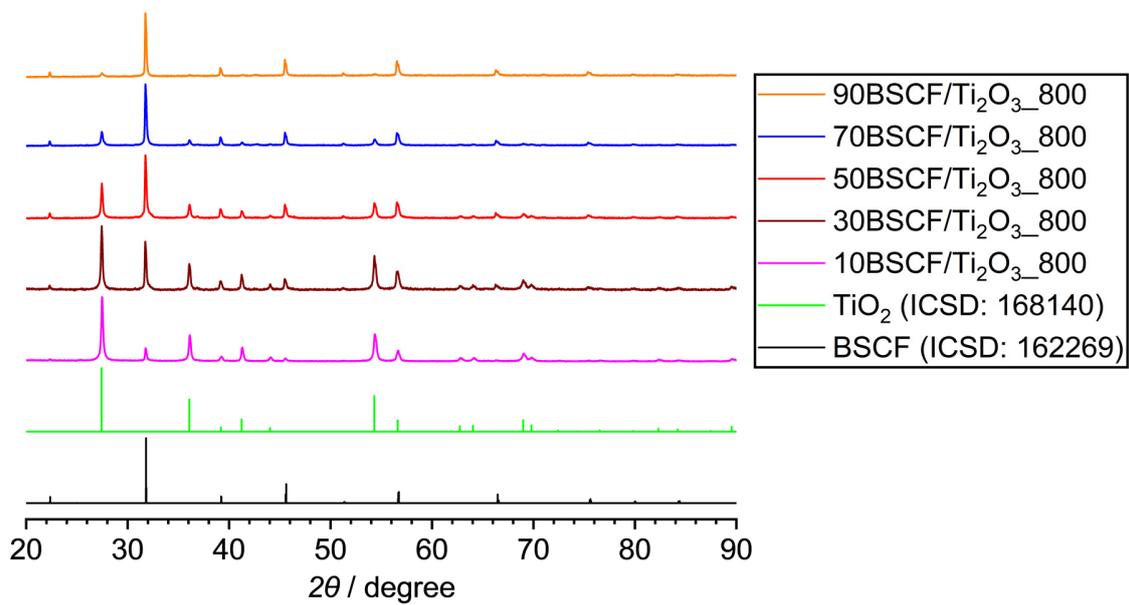
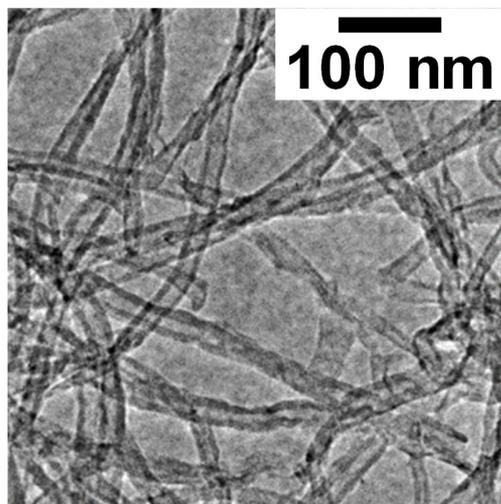


Fig. S9 XRD patterns of 10BSCF/Ti₂O₃_800, 30BSCF/Ti₂O₃_800, 50BSCF/Ti₂O₃_800, 70BSCF/Ti₂O₃_800, and 90BSCF/Ti₂O₃_800.

Table S1 Bulk electrical conductivities of BSCF/Ti₂O₃ samples.

Sample	BSCF composition [wt%]	Annealing temperature [°C]	Conductivity [mS cm ⁻¹]
50BSCF/Ti ₂ O ₃ _PM	50	Physical mixing	0.12
50BSCF/Ti ₂ O ₃ _200	50	200	0.41
50BSCF/Ti ₂ O ₃ _400	50	400	0.31
50BSCF/Ti ₂ O ₃ _600	50	600	0.52
Ti ₂ O ₃ _800	0	800	1.5
10BSCF/Ti ₂ O ₃ _800	10	800	0.92
30BSCF/Ti ₂ O ₃ _800	30	800	0.77
50BSCF/Ti ₂ O ₃ _800	50	800	0.85
70BSCF/Ti ₂ O ₃ _800	70	800	0.30
90BSCF/Ti ₂ O ₃ _800	90	800	0.12
BSCF_800	100	800	0.075

Initial



After 2000 cycles

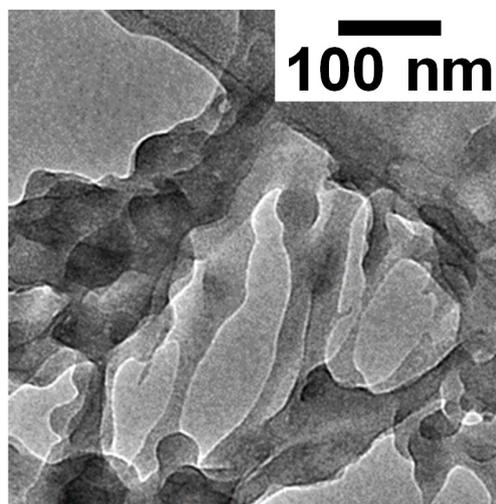


Fig. S10 TEM images of CNT before and after repeated potential cycles.

References

- 1 Y. Sugawara, K. Kamata and T. Yamaguchi, *ACS Appl. Energy Mater.*, 2019, **2**, 956–960.
- 2 K. Sugahara, K. Kamata, S. Muratsugu and M. Hara, *ACS Omega*, 2017, **2**, 1608–1616.
- 3 Y. G. Li, W. Zhou, H. L. Wang, L. M. Xie, Y. Y. Liang, F. Wei, J. C. Idrobo, S. J. Pennycook and H. J. Dai, *Nat. Nanotechnol.*, 2012, **7**, 394–400.