

## PAPER

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# High-efficiency oxygen evolution catalysts: composite hexagonal structure $\text{SrCo}_{1-y}\text{Ni}_y\text{O}_{3-\delta}/\text{Sr}_9\text{Ni}_7\text{O}_{21}^\dagger$

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Transition metal perovskite oxides are regarded as ideal catalysts for the oxygen evolution reaction (OER) owing to the high tunability of the B-site active elements. Among them,  $\text{SrCoO}_3$  has been widely studied due to its high theoretical catalytic performance, but incomplete oxidation of the B-site elements results in poor intrinsic activity. Herein, we prepared a series of  $\text{SrCo}_{1-x}\text{Ni}_x\text{O}_{3-\delta}$  ( $x = 0-0.5$ ) catalysts for the alkaline OER using a simple sol-gel method and optimized their catalytic performance by modulating the Co/Ni ratio and annealing temperature (950 °C and 1050 °C). Among the series,  $\text{SrCo}_{0.6}\text{Ni}_{0.4}\text{O}_{3-\delta}$  (annealed at 950 °C) with a composite hexagonal structure ( $\text{SrCo}_{1-y}\text{Ni}_y\text{O}_{3-\delta}/\text{Sr}_9\text{Ni}_7\text{O}_{21}$ ,  $y = 0.1-0.2$ ) exhibited the best OER activity, achieving an overpotential of 321 mV at 10  $\text{mA cm}^{-2}$  (1 M KOH). The introduction of Ni ions and the presence of  $\text{Sr}_9\text{Ni}_7\text{O}_{21}$  not only enhance the  $\text{Co}^{4+}/\text{Co}^{3+}$  and  $\text{Ni}^{3+}/\text{Ni}^{2+}$  ratios but also promote the generation of more highly oxidative oxygen species ( $\text{O}_2^{2-}/\text{O}^-$ ). Additionally, the abundant  $\text{Ni}^{3+}$  surface facilitates the formation of a highly active NiOOH phase during the OER, leading to a further reduction in the overpotential (after 1000 CV cycles, the overpotential on the nickel foam electrode decreased by 45 mV).

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## 1. Introduction

The oxygen evolution reaction (OER) is a critical process in various energy conversion and storage systems, such as electrochemical water splitting and rechargeable metal-air batteries.<sup>1,2</sup> Its complex intermediate steps involve multiple electron/proton transfers, leading to slow reaction kinetics.<sup>3</sup> Consequently, it is essential to develop OER catalysts that exhibit both high performance and long-term stability. Noble metal-based oxides ( $\text{IrO}_2$ ,  $\text{RuO}_2$ , etc.) show excellent OER activity, but their scarcity and high cost limit their large-scale practical application.<sup>4,5</sup> Among transition metals, cobalt and nickel oxides exhibit water oxidation performance comparable to that of noble metal catalysts under alkaline conditions, making them ideal alternative materials.<sup>6,7</sup>

Currently, transition metal-based OER catalysts mainly include three structural types: layered hydroxide, spinel and perovskite.<sup>8</sup> Perovskite oxides have been widely studied due to their flexible composition and adjustable structure.<sup>9,10</sup> Several

OER activity descriptors have been developed based on the B-site active ions, such as the electron occupancy of the  $e_g$  orbital,<sup>11</sup> metal-oxygen bond covalency<sup>12</sup>, the p-band center of O relative to the Fermi level,<sup>13</sup> etc. Among the diverse perovskite oxides, cubic  $\text{SrCoO}_3$  is predicted to have the highest theoretical OER activity.<sup>14</sup> Due to the incomplete oxidation of Co ions, only oxygen-deficient  $\text{SrCoO}_{3-\delta}$  with a hexagonal  $\text{Sr}_6\text{Co}_5\text{O}_{15}$  structure can be synthesized under normal pressure.<sup>15,16</sup>

Grimaud's research demonstrates that the surface-shared coordination and one-dimensional prism structure of hexagonal perovskites have important effects on the activity and stability of the OER.<sup>17</sup> Wei *et al.* prepared an Fe-doped hexagonal  $\text{Sr}_6(\text{Co}_{0.8}\text{Fe}_{0.2})_5\text{O}_{15}$  (SCF-H), which exhibits markedly better OER activity compared to cubic  $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  (SCF-C). Specifically, hexagonal SCF-H features a higher concentration of surface reactive oxygen species ( $\text{O}_2^{2-}/\text{O}^-$ ), and its O p band center is closer to the Fermi level.<sup>18</sup> Similarly, Lee *et al.* reported a phase transition mechanism from hexagonal  $\text{BaNiO}_3$  to  $\text{Ba}_6\text{Ni}_5\text{O}_{15}$  during the OER. The formation of Ni vacancies optimizes the oxidation state ( $\text{Ni}^{4+} \rightarrow \text{Ni}^{3+}/\text{Ni}^{2+}$ ), thereby enhancing both the OER activity and cycling stability.<sup>19</sup> The above studies have convincingly confirmed that single-phase hexagonal perovskites have great potential in the field of OER catalysis. Composite structure engineering is an

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emerging strategy to enhance the catalytic performance of single-phase perovskites.<sup>20,21</sup> Recently, Wang's team has developed a new 2D descriptor ( $d_B$ ,  $n_B$ ) for predicting the OER activity of perovskites and discovered an unreported hexagonal perovskite  $\text{SrCo}_{0.6}\text{Ni}_{0.4}\text{O}_{3-\delta}$  with high OER activity.<sup>22</sup> However,  $\text{SrCo}_{0.6}\text{Ni}_{0.4}\text{O}_{3-\delta}$  is not a single-phase structure material, making it inappropriate to apply the activity descriptors designed for single-phase perovskites to understand the activity source of this composite catalyst. Furthermore, the formation of such a composite structure originates from the solubility limits of the dopant elements and demonstrates a significant simplicity advantage over alternative fabrication approaches.<sup>23,24</sup>

Here, we have successfully isolated two major hexagonal perovskite structures ( $\text{SrCo}_{1-y}\text{Ni}_y\text{O}_{3-\delta}$ ,  $y = 0.1-0.2$  and  $\text{Sr}_9\text{Ni}_7\text{O}_{21}$ ) in  $\text{SrCo}_{0.6}\text{Ni}_{0.4}\text{O}_{3-\delta}$ . The relationship between the phase composition and surface states of the composite structure ( $\text{SrCo}_{1-y}\text{Ni}_y\text{O}_{3-\delta}/\text{Sr}_9\text{Ni}_7\text{O}_{21}$ ) and the properties of the OER has been investigated. This composite catalyst exhibits superior OER activity compared to pure hexagonal  $\text{SrCoO}_{3-\delta}$ ,  $\text{SrCo}_{0.9}\text{Ni}_{0.1}\text{O}_{3-\delta}$  and  $\text{SrCo}_{1-y}\text{Ni}_y\text{O}_{3-\delta}/\text{NiO}$  composite structures. Ni doping and the presence of SNO not only improve the oxidation state of B-site active elements (Co/Ni) but also introduce a higher concentration of highly oxidative oxygen species ( $\text{O}_2^{2-}/\text{O}^-$ ).  $\text{SrCo}_{1-y}\text{Ni}_y\text{O}_{3-\delta}/\text{Sr}_9\text{Ni}_7\text{O}_{21}$  enhances  $\text{NiOOH}$  formation during the reaction, which reduces the overpotential by 45 mV after 1000 CV cycles. This study provides new insights for the design and development of efficient OER catalysts through multi-metallic synergy and composite structure design.

## 2. Experimental

### 2.1. Catalyst synthesis

A series of catalyst powders  $\text{SrCo}_{1-x}\text{Ni}_x\text{O}_{3-\delta}$  ( $x = 0-0.5$ ) ( $\text{SCNxO}$ ) were prepared at 950 °C and 1050 °C by using the sol-gel method: firstly,  $\text{Sr}(\text{NO}_3)_2$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  with a ratio of  $1:1-x:x$  were completely dissolved in deionized water and stirred at 70 °C for 30 minutes to obtain a precursor solution. Ethylenediaminetetraacetic acid (EDTA) and citric acid (CA) were added as complexing agents, with metal ions: EDTA:CA = 1:1:2. The pH of the solution was adjusted to 7–9 by dropwise adding ammonia solution. The temperature was subsequently raised to 120 °C, and the solution was continuously stirred until it formed a purplish-red gel due to water evaporation. This gel was transferred to a vacuum drying oven at 250 °C and dried for 5 h to obtain a black and fluffy precursor. After simple grinding, the precursor was annealed at 950 °C ( $\text{SCNxO9}$ ) and 1050 °C ( $\text{SCNxO10}$ ) for 6 h at a heating rate of 5 °C  $\text{min}^{-1}$ , respectively. Finally, the black catalyst powders were obtained by fully grinding the product.

### 2.2. Characterization

The phase structures of  $\text{SCNxO}$  catalysts were characterized using an Anton Paar XRDynaMic500 X-ray diffractometer, and

the radiation source was Cu K $\alpha$  ( $\lambda = 0.154$  nm). The XRD patterns were Rietveld refined using GSAS-II software.<sup>25</sup> The Raman tests were carried out on a Renishaw inVia Raman spectrometer with a 532 nm laser. The microstructure of the catalyst was studied by scanning electron microscopy (SEM, Tescan-VEGA3, Czechia). The surface elemental distribution of the catalyst was analyzed using an electron probe microanalyzer (EPMA, Shimadzu EPMA-1720H) equipped with energy-dispersive spectroscopy (EDS) and wavelength-dispersive spectroscopy (WDS). The surface chemical state of the catalyst was analyzed by X-ray photoelectron spectroscopy (XPS Thermo Scientific K-Alpha). TEM images were obtained using a FEI-Tecna G2 F30 S-Twin transmission electron microscope with an operating voltage of 200 kV. The Micromeritics ASAP 2460 automatic specific surface and porosity analyzer was used to measure the specific surface area of the catalyst powders based on the Brunauer–Emmett–Teller (BET) method.

### 2.3. Electrochemical measurements

The preparation process of the working electrode was as follows: 7 mg catalyst powders and 70  $\mu\text{L}$  Nafion solution (20 wt%) were placed in a 2 mL ethanol solution (ethanol: deionized water = 7:3), followed by ultrasonic treatment for 1 h. The 10  $\mu\text{L}$  catalyst ink drop prepared above was coated on a glassy carbon electrode ( $d = 5$  mm) and dried in the air for 1 h. The mass load of the catalyst was approximately 0.173  $\text{mg}_{\text{oxide}} \text{cm}^{-2}$ .

Electrochemical measurements were performed in an  $\text{O}_2$ -saturated 1 M KOH solution using a standard three-electrode configuration on an electrochemical workstation (CHI 760E). The Hg/HgO electrode and graphite rod were used as the reference electrode and the counter electrode, respectively. The working electrodes were subjected to 50 cyclic voltammetry (CV) tests in a potential range of 0–0.8 V (vs. Hg/HgO) to activate the catalysts. Then linear sweep voltammetry curves (LSV) of the OER were obtained at a scanning rate of 5  $\text{mV s}^{-1}$ . Electrochemical impedance spectroscopy (EIS) tests were performed from  $10^{-5}$  to  $10^{-1}$  Hz at an applied potential of 0.66 V (vs. Hg/HgO) with an amplitude of 5 mV. Double-layer capacitance ( $C_{\text{dl}}$ ) tests were evaluated by CV measurements at scan rates of 20, 40, 60, 80, and 100  $\text{mV s}^{-1}$  at 0.12–0.22 V (vs. Hg/HgO), and the electrochemically active surface area (ECSA) of the catalysts was obtained using the following formula:  $\text{ECSA} = C_{\text{dl}}/C_s$ , where specific capacitance  $C_s = 60 \mu\text{F cm}^{-2}$  (referred to the reported value of perovskite oxide in 1 M KOH solution). All measured potential data were manually calibrated with 95% IR to compensate for solution resistance and then were converted to the reversible hydrogen electrode (RHE) scale using the following formula:  $E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.9122$  V.

The stability tests were divided into two parts: one is accelerated durability testing (ADT), and the catalyst stability was evaluated by performing 1000 CV tests at a scan rate of 100  $\text{mV s}^{-1}$  at 0–0.8 V (vs. Hg/HgO). The second method was durability testing by chronopotentiometry. The working electrodes were changed to Ni-foam coated with the catalyst: the ink was made by ultrasonic mixing of 5 mg catalyst powders, 50  $\mu\text{L}$  Nafion

solution and 1 mL ethanol, and 400  $\mu\text{L}$  of the ink was coated on Ni-foam ( $1 \times 1 \times 0.1$  cm). The mass load of the catalyst was about  $1.9 \text{ mg}_{\text{oxide}} \text{ cm}^{-2}$ .

### 3. Results and discussion

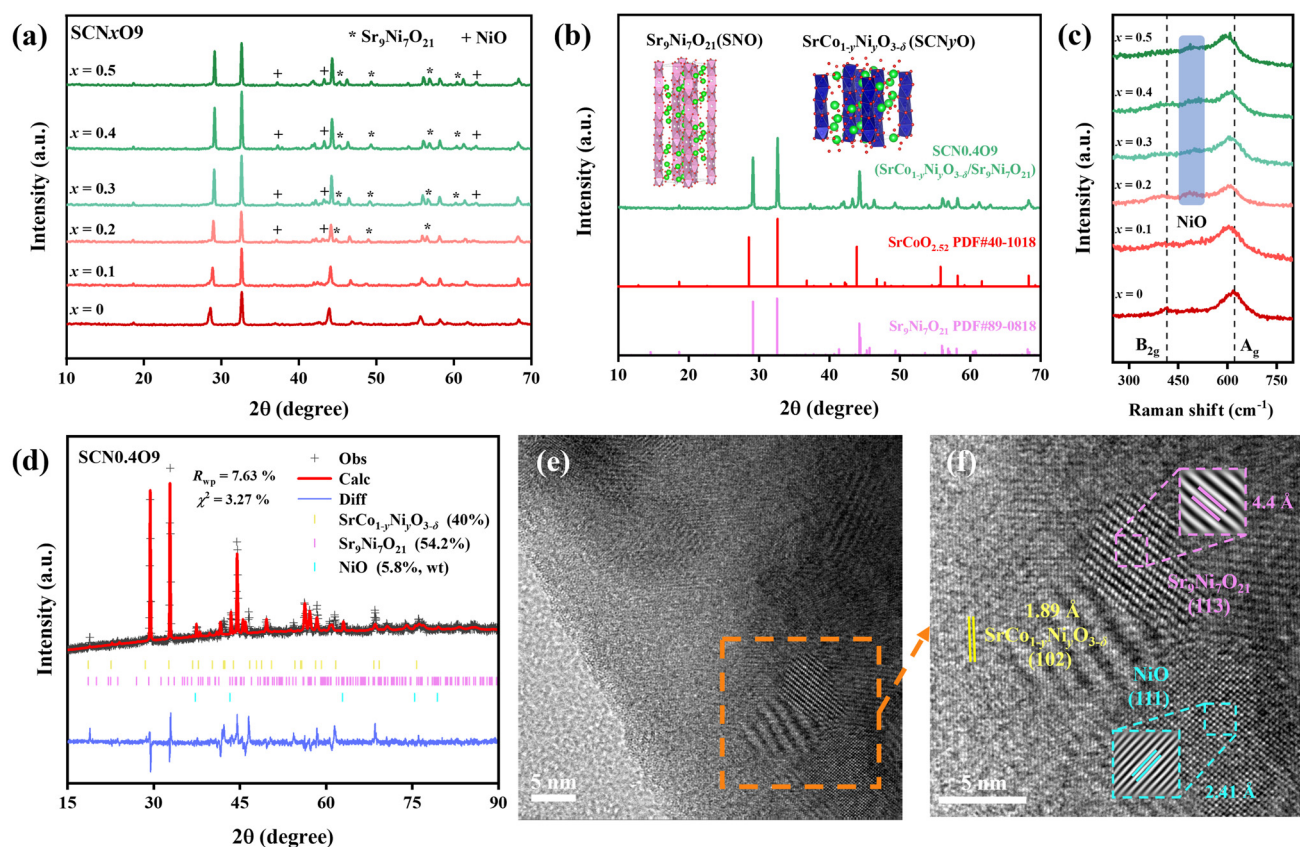
#### 3.1. Crystal structure and the microstructure

Fig. 1a shows the XRD patterns of  $\text{SCN}_x\text{O}_9$  ( $x = 0-0.5$ ) series catalysts. The initial  $\text{SrCoO}_{3-\delta}$  (SCO) exhibits a hexagonal structure indexed to PDF#40-1018 ( $\text{SrCoO}_{2.52}$ ),<sup>26</sup> and Ni doping does not induce a phase transition. When the Ni content  $x$  reaches 0.2,  $\text{SCN}_x\text{O}_9$  forms a composite structure consisting of  $\text{SrCo}_{1-y}\text{Ni}_y\text{O}_{3-\delta}$  ( $y = 0.1-0.2$ ) ( $\text{SCN}_y\text{O}$ ) and  $\text{Sr}_9\text{Ni}_7\text{O}_{21}$  (SNO, PDF#89-0819), with a minor presence of NiO (PDF#78-0423).<sup>27</sup> SNO has a hexagonal structure similar to SCO (Fig. 1b) and NiO has a cubic structure with the space group  $Fm\bar{3}m$ . However, when the annealing temperature is increased to  $1050^\circ\text{C}$ , these two phases appear only when the Ni content  $x$  exceeds 0.3 (Fig. S1†). Furthermore, the number of SNO characteristic peaks decreases significantly, while the intensity of NiO peaks increases markedly. The higher annealing temperature increases the solid solubility of Ni in SCO and the content of the NiO phase and inhibits the formation of the SNO phase. These phenomena are consistent with the study of

the Sr–Ni–O system phase diagram: within the temperature range of  $800^\circ\text{C}$ – $1030^\circ\text{C}$ , only SNO and NiO can exist stably. When the temperature exceeds  $1030^\circ\text{C}$ , SNO will decompose into SrO and NiO.<sup>28</sup> Therefore, for  $x = 0.3-0.5$ , the content of SNO in  $\text{SCN}_x\text{O}_9$  is significantly reduced, leading to the formation of a composite structure primarily consisting of  $\text{SCN}_y\text{O}$  ( $y = 0.2-0.3$ ) and NiO.

The phase structures of  $\text{SCN}_x\text{O}_9$  have been further analyzed by Raman spectroscopy (Fig. 1c). The peaks at approximately  $429 \text{ cm}^{-1}$  and  $629 \text{ cm}^{-1}$  come from the  $B_{2g}$  and  $A_g$  vibration modes of hexagonal SCO,<sup>29</sup> and these exhibit a slight blue shift with the partial substitution of Co by Ni. SNO does not lead to the emergence of new Raman characteristic peaks due to the similar hexagonal structure. The new peak gradually appearing near  $500 \text{ cm}^{-1}$  arises from the stretching vibration of the Ni–O bond in NiO.<sup>30</sup> The XRD pattern of  $\text{SCN}_{0.4}\text{O}_9$  has been refined using the Rietveld method (Fig. 1d), which further confirmed the  $\text{SCN}_y\text{O}$ /SNO composite structure. Fig. 1e and f display the TEM images of  $\text{SCN}_{0.4}\text{O}_9$ . The lattice spacings of  $4.4 \text{ \AA}$  and  $1.89 \text{ \AA}$  correspond to the (113) plane of SNO and the (102) plane of  $\text{SCN}_y\text{O}$ , respectively. The lattice spacing of  $2.41 \text{ \AA}$  corresponds to the (111) plane of NiO.

SEM images reveal the microstructure of  $\text{SCN}_x\text{O}$  ( $x = 0-0.5$ ) series catalysts, as shown in Fig. 2 and S2.† All samples consist of micron-scale granules. The surfaces of the  $\text{SCN}_x\text{O}_{10}$  series



**Fig. 1** (a) XRD patterns of  $\text{SCN}_x\text{O}_9$  ( $x = 0-0.5$ ). (b) XRD patterns of  $\text{SCN}_{0.4}\text{O}_9$ ,  $\text{SrCoO}_{2.52}$  and  $\text{Sr}_9\text{Ni}_7\text{O}_{21}$ . (c) Raman spectra of  $\text{SCN}_x\text{O}_9$  ( $x = 0-0.5$ ). (d) Rietveld refinement results of the XRD pattern of  $\text{SCN}_{0.4}\text{O}_9$ . (e and f) TEM images of  $\text{SCN}_{0.4}\text{O}_9$ .

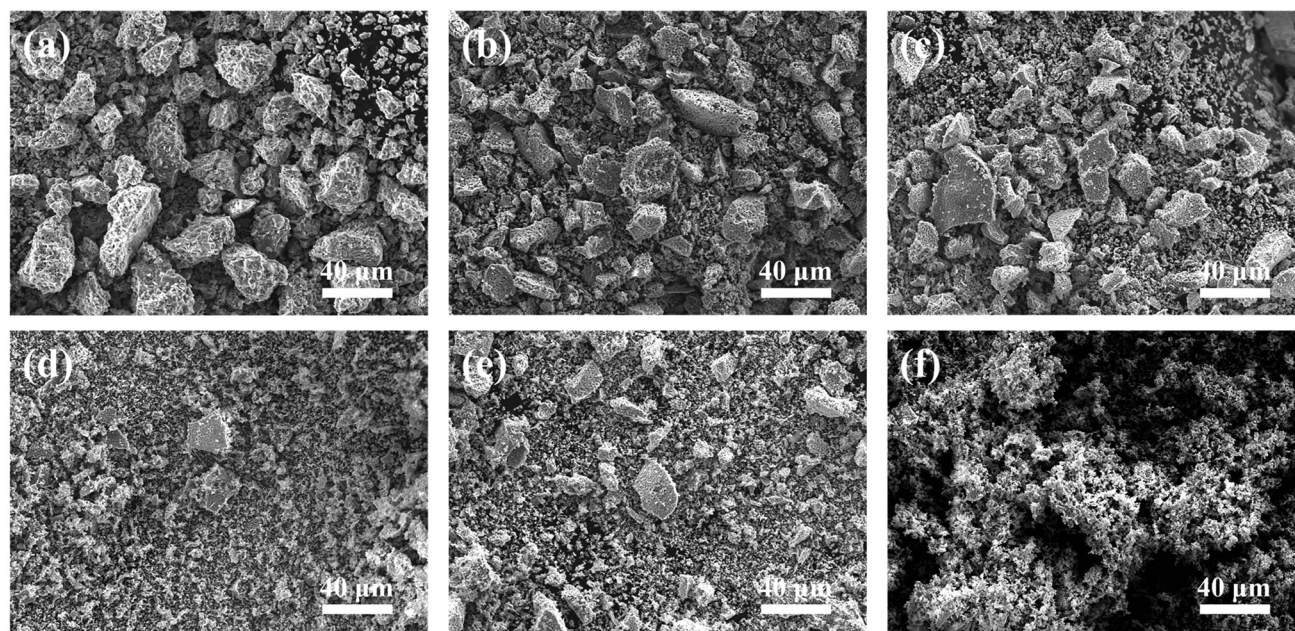


Fig. 2 SEM images of SCN<sub>x</sub>O<sub>9</sub> series catalysts: (a)  $x = 0$ , (b)  $x = 0.1$ , (c)  $x = 0.2$ , (d)  $x = 0.3$ , (e)  $x = 0.4$ , and (f)  $x = 0.5$ .

are denser than those of the SCN<sub>x</sub>O<sub>9</sub> series due to the higher annealing temperature. At the same annealing temperature, the increase of Ni doping leads to the decrease of catalyst particle size and the increase of surface pore number. This change exposes more active sites on the catalyst surface for an efficient OER. Furthermore, we measured the BET specific surface area of the SCN<sub>x</sub>O<sub>9</sub> series catalysts (Fig. S3†), and the results are consistent with the SEM observations. SCN<sub>0.5</sub>O<sub>9</sub> exhibits the largest BET specific surface area, approximately five times that of SCO. EDS mappings of SCN<sub>0.4</sub>O<sub>9</sub> show that the four elements Sr, Co, Ni and O are evenly distributed within individual particles (Fig. S4†). To further investigate the distribution of newly formed SNO and NiO, the elements on the surface of SCN<sub>0.4</sub>O<sub>9</sub> particles were analyzed by WDS (Fig. S5†). The SNO phase and the NiO phase, represented by dark blue and red, respectively, are uniformly distributed on the catalyst powders' surface, with no evident segregation.

### 3.2. OER catalytic performance

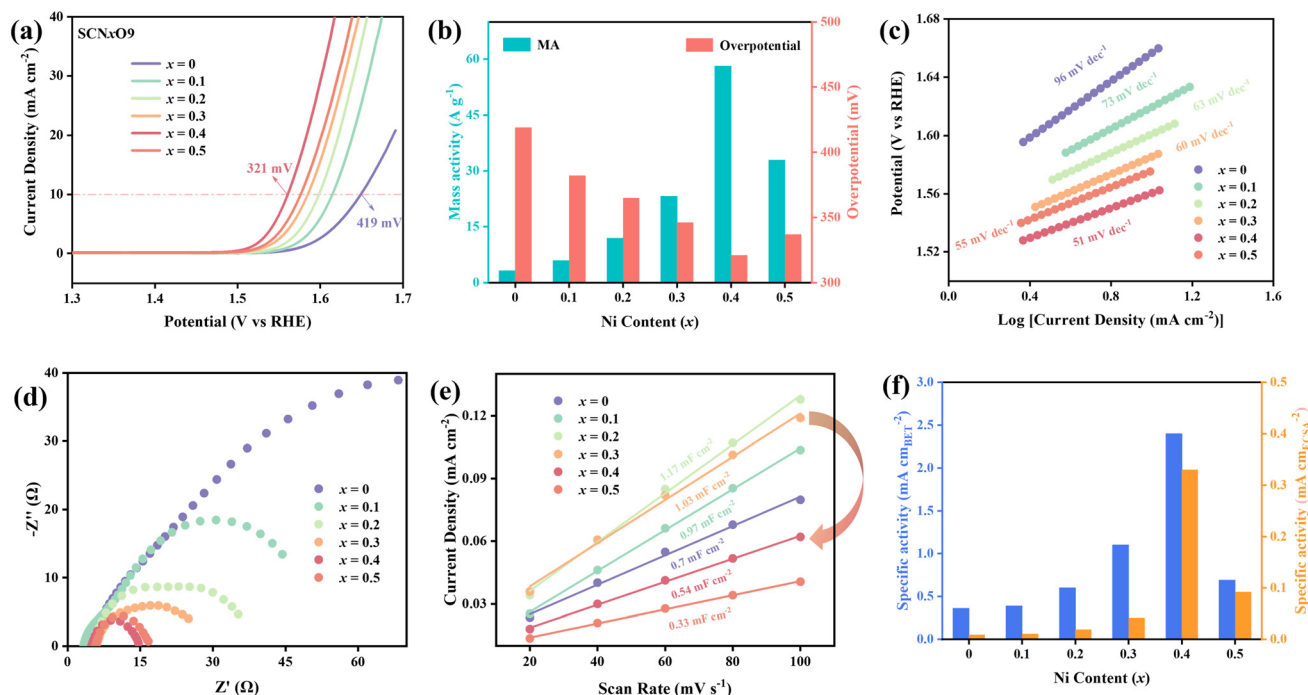
The LSV curves of the SCN<sub>x</sub>O<sub>9</sub> ( $x = 0-0.5$ ) series catalysts are shown in Fig. 3a. The overpotential of the catalysts at 10 mA cm<sup>-2</sup> decreases with the increasing Ni doping amount. Among them, SCN<sub>0.4</sub>O<sub>9</sub> with a composite structure (SCN<sub>y</sub>O/SNO) exhibits the best OER activity (321 mV), significantly better than the initial SCO (419 mV) and single-phase SCN<sub>0.1</sub>O<sub>9</sub> (382 mV). This composite perovskite catalyst demonstrates comparable or even superior performance relative to recently reported Co and Ni based oxides (Table S1†). Furthermore, the mass activity of the SCN<sub>x</sub>O<sub>9</sub> series catalysts was calculated (Fig. 3b). SCN<sub>0.4</sub>O<sub>9</sub> showed 18.7 times higher mass activity than SCO, indicating its greater potential for commercial applications. The Tafel slope is an important tool for studying OER kinetics. As shown in Fig. 3c, the Ni-doped SCN<sub>x</sub>O<sub>9</sub> series

exhibits a reduced Tafel slope value, which indicates a faster kinetic process. Specifically, the rate-determining step (RDS) of the OER can be calculated using the formula  $(59 \text{ mV dec}^{-1})/(n' + \alpha)$ , where  $\alpha$  is the symmetry/transfer coefficient (usually taken as 0.5) and  $n'$  is the number of single electron transfer steps before the RDS.<sup>31,32</sup> The Tafel slope of the initial SCO is 96 mV dec<sup>-1</sup>, close to the characteristic value of 120 mV dec<sup>-1</sup>, suggesting that its RDS primarily follows the first electron transfer process ( $* + \text{OH}^- \rightarrow \text{OH}^* + \text{e}^-$ ); the Tafel slope of SCN<sub>0.4</sub>O<sub>9</sub> is 51 mV dec<sup>-1</sup>, approaching the characteristic value of 40 mV dec<sup>-1</sup>, indicating that the second electron transfer process ( $\text{OH}^* + \text{OH}^- \rightarrow \text{O}^* + \text{O}_2 + \text{e}^-$ ) dominates its RDS. Additionally, SCN<sub>0.4</sub>O<sub>9</sub> shows the smallest surface charge transfer resistance ( $R_{\text{ct}}$ ) (Fig. 3d).

The ECSA of the SCN<sub>x</sub>O<sub>9</sub> series catalysts have been calculated through  $C_{\text{dl}}$  tests (Fig. 3e and S6, S7†). A lower amount of Ni doping ( $x = 0.1-0.3$ ) results in an increase in ECSA. Surprisingly, the ECSA of SCN<sub>0.4</sub>O<sub>9</sub>, which exhibits the best OER activity in the series, is sharply reduced compared to SCN<sub>0.3</sub>O<sub>9</sub>. BET test results suggest that this phenomenon is not due to a reduction in the specific surface area. Relevant studies indicate that this may be because the Ni<sup>2+</sup> species in the catalyst are non-conductive within the non-faradaic potential range, leading to inaccuracies in the  $C_{\text{dl}}$  tests.<sup>33,34</sup> Therefore, the ECSA cannot accurately reflect the true number of active sites on the sample surface. However, both the BET area specific activity and the ECSA specific activity of the SCN<sub>x</sub>O<sub>9</sub> series exhibit the same trend (Fig. 3f), with the SCN<sub>0.4</sub>O<sub>9</sub> composite demonstrating the highest intrinsic OER activity in the series.

### 3.3. Relationship between surface states and OER activity

The XPS spectra of Sr, Co and Ni in the SCN<sub>x</sub>O<sub>9</sub> ( $x = 0-0.5$ ) series catalysts are shown in Fig. 4. The two main peaks in the



**Fig. 3** OER activity of SCN $x$ O9 ( $x = 0–0.5$ ) series catalysts: (a) LSV curves, (b) overpotential at 10 mA cm $^{-2}$  current density and mass activity at 1.55 V (vs. RHE) potential, (c) Tafel slopes, (d) Nyquist plots, (e)  $C_{dl}$  values (obtained by linear fitting of current density differences ( $\Delta j/2$ ) at different scanning rates in the non-Faraday interval), (f) BET area specific activity and ECSA specific activity at 1.55 V (vs. RHE) (based on the BET surface area and the ECSA standardized current density, respectively).

Co 2p spectrum can be deconvoluted into two sets of doublets: the peaks at 780.1 eV and 795.1 eV come from Co $^{3+}$  ions, while the peaks at 781.6 eV and 796.6 eV belong to Co $^{4+}$  ions (Fig. 4a).<sup>35</sup> As the Ni content  $x$  increases from 0 to 0.1, the Co $^{4+}$ /Co $^{3+}$  ratio significantly increases, after which it remains relatively constant (Fig. 4d). This indicates that the Ni doping effect can enhance the average oxidation state of Co, which is beneficial for improving the intrinsic OER activity of Co-based oxides.<sup>36</sup> The peak fitting results of Ni are shown in Fig. 4b. For  $x = 0.1–0.5$ , both Ni $^{3+}$  ions (856 eV and 873.3 eV) and Ni $^{2+}$  ions (854.5 eV and 871.8 eV) coexist.<sup>37</sup> Two Ni-containing phases (SNO and NiO) are present in the catalysts. The increased Ni $^{3+}$  ions originate from SNO, as NiO can only provide Ni $^{2+}$  species. The composite SCN0.4O9 surface possesses the highest Ni $^{3+}$ /Ni $^{2+}$  ratio (Fig. 4d), which means the highest proportion of SNO. Compared with Ni $^{2+}$ , the higher-valent Ni $^{3+}$  has a stronger OH $^{-}$  adsorption capacity. Consequently, the enhancement of the Ni oxidation state can strengthen the adsorption of reaction intermediates on the sample surface.<sup>38</sup> In the previous OER test, SCN0.4O9 exhibited the lowest overpotential and the highest specific activity among the series. The introduction of Ni ions and the presence of SNO in its composite structure optimize the electronic structure of surface active elements (Co/Ni), thereby enhancing the intrinsic activity. This plays a dominant role in enhancing the OER catalytic performance of the SCN $x$ O9 series samples. The fitting results of the Sr 3d spectra reveal two types of Sr on the surface of the SCN $x$ O9 series (Fig. 4c): the lattice Sr with

lower binding energy and the surface Sr with higher binding energy (SrO or Sr(OH) $_2$ ).<sup>39</sup> Furthermore, compared with SCO, the composite SCN0.4O9 surface contains a higher concentration of highly oxidative oxygen species (O $_2^{2-}$ /O $^{-}$ ) (Fig. 4e). Many studies have shown that highly oxidized oxygen (O $_2^{2-}$ /O $^{-}$ ) plays an important role in the OER process.<sup>40,41</sup>

To further determine the contribution of the SCN $y$ O/SNO composite structure to OER activity, electrochemical tests were conducted on the SCN $x$ O10 ( $x = 0–0.5$ ) series catalysts (Fig. 5a). Although their OER activity improved with Ni doping, the extent of performance enhancement is not as significant as the SCN $x$ O9 series. Fig. 5b presents the LSV curves for SCN0.4O9, SCN0.4O10, and pure NiO, and it has been found that the catalytic activity of the SCN $y$ O/SNO composite structure is significantly better than that of SCN0.4O10 (372 mV) and pure NiO (410 mV).

### 3.4. Catalytic stability and surface reconstruction during the OER

The catalytic stability of the SCN0.4O9 composite sample on a Ni-foam substrate was assessed by accelerated durability testing (ADT) and chronopotentiometry (CP). As shown in Fig. S8,<sup>†</sup> the OER activity of pristine nickel foam is significantly lower than that of SCN0.4O9-loaded Ni-foam and SCN0.4O9-coated GC. Therefore, replacing GC with Ni-foam will not affect the reliability of the stability test results. Fig. 6a and b show the ADT results for SCO9 and SCN0.4O9, where both materials exhibit enhanced OER activity after ADT. The

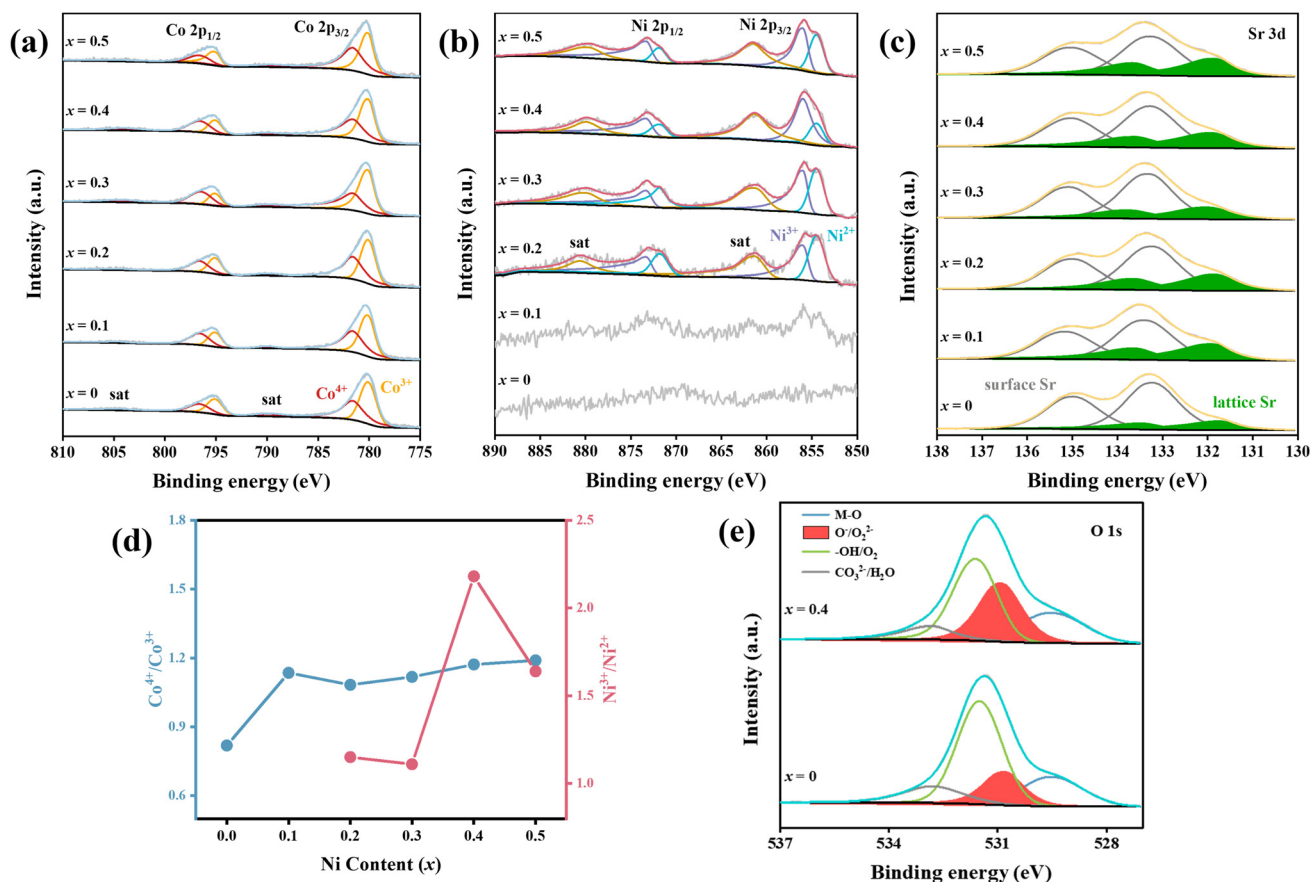


Fig. 4 XPS spectra of SCN<sub>x</sub>O<sub>9</sub> ( $x = 0-0.5$ ) series catalysts: (a) Co 2p, (b) Ni 2p, and (c) Sr 3d. (d) Curves of Co<sup>4+</sup>/Co<sup>3+</sup> and Ni<sup>3+</sup>/Ni<sup>2+</sup> ratios with the increase of Ni content. (e) O 1s XPS spectra of SCO<sub>9</sub> and SCN<sub>0.4</sub>O<sub>9</sub>.

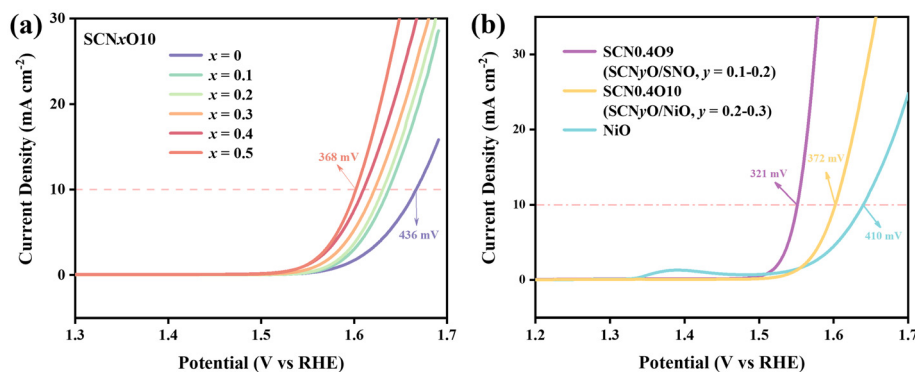
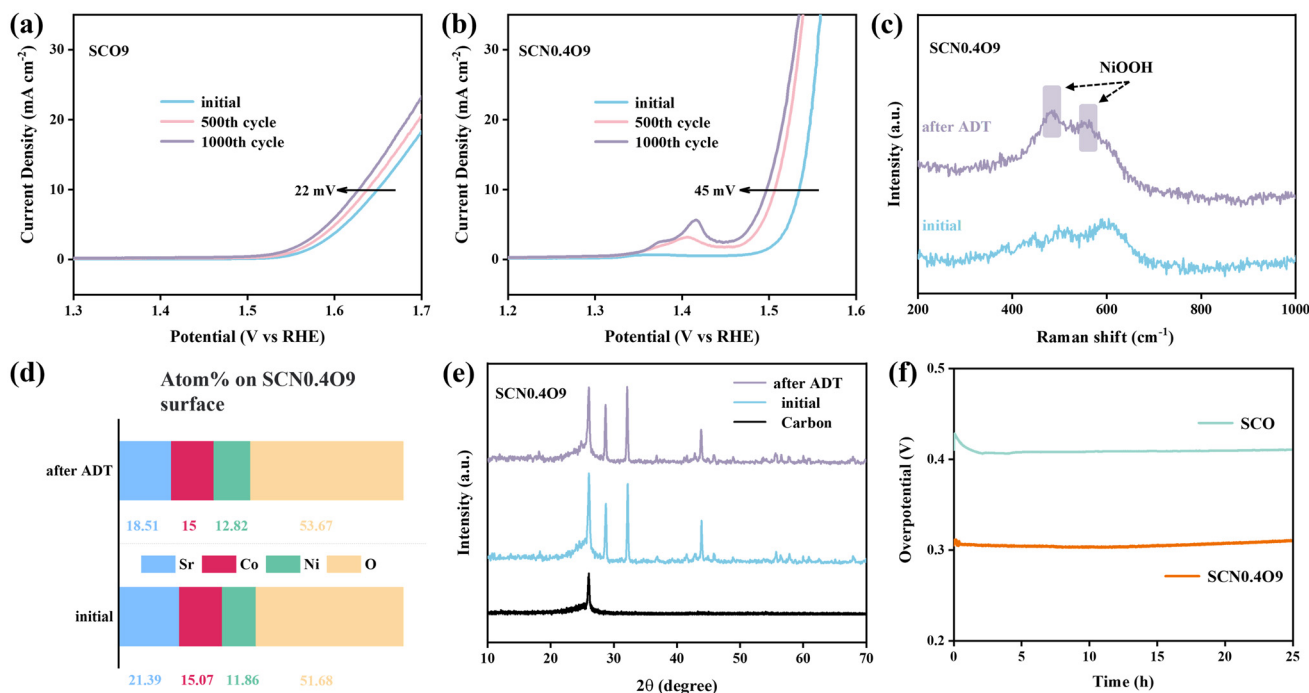


Fig. 5 (a) LSV curves of SCN<sub>x</sub>O<sub>10</sub> series catalysts and (b) LSV curves of SCN<sub>0.4</sub>O<sub>9</sub>, SCN<sub>0.4</sub>O<sub>10</sub> and NiO (the NiO sample is a commercial product: purity >99.5% and particle size <30 nm. The preparation process of catalyst ink and the ink load of the GC electrode are consistent with those of SCN<sub>x</sub>O).

overpotential of SCO<sub>9</sub> decreased by 22 mV at 10 mA cm<sup>-2</sup>, while the overpotential of the SCN<sub>0.4</sub>O<sub>9</sub> composite reduced by up to 45 mV. Previous studies have indicated that this improvement may be attributed to surface reconstruction during the OER.<sup>42,43</sup> The Raman spectra of SCN<sub>0.4</sub>O<sub>9</sub> after ADT reveal two new peaks at 473 and 555 cm<sup>-1</sup> (Fig. 6c), which are characteristic signals of NiOOH.<sup>44</sup> This suggests that Ni on the catalyst

surface gradually combines with OH<sup>-</sup> in the electrolyte to form a highly active NiOOH phase during the OER. The high ratio of Ni<sup>3+</sup>/Ni<sup>2+</sup> on the surface of SCN<sub>0.4</sub>O<sub>9</sub> facilitates this transformation more easily compared to other catalysts in the series.<sup>45</sup> Additionally, this reconstruction is typically accompanied by the dissolution of surface A-site cations.<sup>46</sup> As shown in Fig. 6d, the atomic fraction of Sr on the initial surface is 21.39%,



**Fig. 6** LSV curves of (a) SCO9 and (b) SCN0.4O9 after initial and different cycles during ADT; the working electrode is a Ni-foam supported catalyst. (c) Raman spectra of SCN0.4O9 before and after ADT. (d) Atomic fraction of Sr, Co, Ni and O obtained by EDS mapping of SCN0.4O9 before and after ADT. (e) XRD patterns of carbon paper loaded with SCN0.4O9 before and after ADT; the preparation process and the coating amount of catalyst ink were consistent with those of the foam nickel electrode. (f) CP curves of SCO9 and SCN0.4O9 at 10 mA cm<sup>-2</sup> current density.

which decreases to 18.51% after ADT. The relative intensity of WDS mapping of Sr also decreased significantly after ADT (Fig. S9†), further confirming the leaching of Sr ions. Sr-deficient surfaces facilitate exposure to more B-site active elements (Co/Ni), and the surface morphology of SCN0.4O9 does not change significantly before and after ADT. Fig. 6e displays the XRD patterns of SCN0.4O9 before and after ADT, with no additional impurity peaks appearing, indicating that the main structure remains intact. This composite structure (SCNyO/SNO) exhibits good structural stability and catalytic stability.

The XPS spectra of SCN0.4O9 on the carbon paper before and after ADT have been acquired, as illustrated in Fig. S10.† The Sr 3d spectral peak exhibits a notable shift toward the lower binding energy region, accompanied by a slight reduction in intensity (Fig. S10a†). This indicates a reduction in the concentration of surface Sr species, consistent with the EDS and WDS results, indicating that Sr<sup>2+</sup> ions on the sample surface are slightly leached during the OER cycle. Furthermore, the leaching process promotes the exposure of deeper Co sites, resulting in a significant increase in the Co signal intensity on the sample surfaces after ADT (Fig. S10b†). The Co 2p spectral peaks exhibit no significant shift after ADT, suggesting that the surface active Co sites possess good chemical stability. In the Ni 2p spectrum (Fig. S10c†), the proportion of Ni<sup>2+</sup> ions is significantly reduced after ADT, while the proportion of Ni<sup>3+</sup> ions shows a slight increase. This could be attributed to the formation and aggregation of the NiOOH

active phase. The deconvolution of the O 1s spectrum indicates that the content of -OH species on the surface of SCN0.4O9 significantly increases after ADT (Fig. S10d†), further confirming the presence of NiOOH. The catalytic performance of SCN0.4O9 does not significantly deteriorate during 25 h operation, as shown in Fig. 6f. Based on stability studies, the surface B-site element of SCN0.4O9 is activated by the slight leaching of Sr ions, and the formation of highly active hydroxyl oxides further promotes OER performance.

## 4. Conclusion

In this study, we have successfully synthesized a series of SrCo<sub>1-x</sub>Ni<sub>x</sub>O<sub>3-δ</sub> ( $x = 0-0.5$ ) (SCNxO) catalysts and systematically investigated the correlation between their phase composition and OER activity. The initial SCO and SCN0.1O9 (annealed at 950 °C) exhibit a hexagonal single-phase structure. For compositions with  $x = 0.2-0.5$ , incorporation of excess Ni ions leads to the formation of a SrCo<sub>1-y</sub>Ni<sub>y</sub>O<sub>3-δ</sub>/Sr<sub>9</sub>Ni<sub>7</sub>O<sub>21</sub> composite hexagonal structure. This composite structure increases the average oxidation states of Co and Ni on the surface and introduces more active oxygen species (O<sub>2</sub><sup>2-/O</sup>). Notably, the SCN0.4O9 composite demonstrates the lowest overpotential of 321 mV and the smallest Tafel slope of 51 mV dec<sup>-1</sup>, significantly outperforming both SCO and pure-phase SCN0.1O9. The high Ni<sup>3+</sup>/Ni<sup>2+</sup> ratio in SCN0.4O9 promotes the formation of a highly active NiOOH phase during the OER process,

further enhancing its catalytic performance. Furthermore, due to the high-temperature decomposition of SNO, SCN<sub>0.4</sub>O<sub>10</sub> (annealed at 1050 °C) transforms into a SCN<sub>y</sub>O/NiO composite structure and has poor OER activity.

## Author contributions

Xiaolong Yang: conceptualization, investigation, writing – original draft and writing – review & editing. Hongyuan Song: writing – review & editing, investigation, supervision, and conceptualization. Ruihang Yao: investigation. Haorong Wu: investigation. Kun Dong: investigation. Liangwei Chen: investigation. Bin Liu: investigation. Zhenhua Ge: investigation. Lan Yu: supervision, project administration, resources, visualization, and review & editing.

## Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

## Conflicts of interest

There are no conflicts to declare.

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