Oxygen-Evolution Activity of p–n Heterojunction NiO–SnO₂ Ceramic on Ti Substrate Fabricated Using a Simple Layer-by-Layer Method

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ABSTRACT: To expand the application of p–n heterojunction NiO–SnO₂ ceramic materials from gas sensors and photoelectrocatalysts to oxygen-evolution reaction (OER) catalysts, we fabricated two NiO–SnO₂ ceramics on a Ti plate (NSCTs) using a simple layer-by-layer method. The prepared NSCTs (NSCT-480 and NSCT-600) were characterized and analyzed by scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), diffuse reflectance ultraviolet–visible spectroscopy (DRUV–vis), and X-ray photoelectron spectroscopy (XPS). The OER activity and stability were measured by linear sweep voltammetry, cyclic voltammetry, chronoamperometry, amperometric i–t curve, and chronopotentiometry in a 1.0 mol/L NaOH solution at normal temperature and pressure. After 500 cycles, the lower overpotential (η = 194 mV at 1 mA/cm²) indicated that NSCT-600 offered adequate performance as an OER electrocatalyst. Moreover, the changes observed with cyclic voltammetry, SEM, XRD, and XPS during the OER test revealed that the redox cycle of Ni²⁺/Ni³⁺, morphology, and crystal faces of NiO and SnO₂ were three critical factors. The data proved that the NiO–SnO₂ ceramic is a stable OER electrocatalyst. The results of this study will provide a guide for the design and fabrication of p–n heterojunction metal-oxide ceramic electrocatalysts with a high OER performance.

1. INTRODUCTION

Ceramics are widely used in the fields of chemistry, electronics, and biomedical engineering because of their high mechanical strength, hardness, and chemical stability, as well as their optical, electrical, and magnetic performances. Among them, oxide-based ceramics are particularly interesting, as they can be used to prepare gas-separation materials, solar energy conversion materials, anode materials for solid-oxide fuel cells, ferromagnetic materials, biomedical materials, etc. Further, p–n heterojunction oxides have been the subject of considerable study in the field of gas sensors and photoelectrocatalysts. Tseng et al. synthesized NiO/SnO₂ hybrid nanowires using a facile two-step route combining vapor deposition processes. The fabricated nanowires exhibited a higher sensitivity to NO₂ gas at ppm concentrations. More recently, Jayababu et al. found that NiO semishielded SnO₂ p–n heterojunction sensors, which were prepared by coprecipitation and the sol–gel method, exhibited an excellent response to ethanol at room temperature. Under visible light, the photogenerated electron–hole pairs of the p–n heterojunction semiconductor oxides degraded the organic pollutants in wastewater, and split water into hydrogen and oxygen. Zou et al. found that a p–n ZnO–BiO₃ heterojunction prepared by interfacial engineering had excellent photodegradation performance equal to that of RhB. A SnO₂/TiO₂ film, which was fabricated using a simple hydrothermal method, proved capable of the photoelectrocatalytic degradation of methylene blue in aqueous solution under UV-light-emitting diode (UV-LED) light irradiation. In NiCeO₃, the introduced Ni²⁺/³⁺ species could create a p–n junction to improve the photoelectrochemical activation for water oxidation. Recently, a p–n Co₃O₄/TiO₂/Si heterojunction photoanode based on metal–organic frameworks exhibited good water-splitting performance. However, there have been relatively few studies addressing the application of p–n heterojunction ceramics to water electrocatalysis.

With the ongoing development of the global economy and the increase in the population, energy demand will continue to increase in the near future. As well as being one of the ideal sources of energy, hydrogen can be obtained easily through electrocatalytic water-splitting. This involves a hydrogen-evolution reaction (HER) and an oxygen-evolution reaction (OER) during the water-splitting, with the four-electron electrochemical OER being a bottleneck preventing water oxidation. The prohibitive cost, scarce reserves, and unsatisfactory stability of precious metal oxides (IrO₂ and RuO₂) hinder the large-scale production of H₂ through water electrolysis, although they have been successfully applied to OER. Due to their low price and abundance, first-row
transition metals and compounds have been used to develop electrocatalysts with a high OER performance. Many transition metal (hydro)oxides were synthesized and studied in relation to OER under various pH conditions.17−21 Wang et al.22 designed and fabricated Co3O4−x-carbon@Fe2−yCoyO3 hollow polyhedrons using a metal−organic framework-derived method and found that the synthesized electrocatalyst had a lower overpotential and a higher current density than Co3O4−x-carbon and pure Co3O4 hollow polyhedrons. Mu et al.23 found that the surface reconstruction of cobalt phosphides could accelerate the OER. Tian et al.24 constructed Ni3N−NiMoN p−n heterostructures through the nitridation of Ni−Mo−O precursors in an NH3 atmosphere. Among the heterostructures, Ni3N and NiMoN had a high OER and HER activities, respectively. A NiTe/NiS electrocatalyst constructed using an interface engineering process exhibited excellent OER performance under alkaline conditions.25 Recently, cheap FeP and Fe3O4 nanoparticles embedded in N,P-doped microporous carbon nanofibers were found to exhibit robust OER catalytic activity and stability.26 More recently, a three-dimensional (3D) free-standing p−n heterojunction FeNi−LDH/CoP/CC electrode was designed by Zai et al., who adopted an electrochemical deposition technique.27 Relative to FeNi−LDH/CC and CoP/CC, the constructed electrode exhibited significant OER activity. Zai’s research was considered a milestone in the use of a p−n heterojunction material as an OER electrocatalyst.28

2. RESULTS AND DISCUSSION

2.1. Physical Characterization. 2.1.1. SEM Image Analysis of NSCTs. Figure 1 shows the SEM images of NSCT-480 (a,b) and NSCT-600 (c,d). Figure 1a,c shows that amorphous and crystal oxides possibly coexist on the surface. Many regular crystals were observed when the images were magnified 100 000×, indicating that crystal NiO is formed on the NSCTs.29 Compared to those of NSCT-480, the NiO crystals of NSCT-600 were more regular (Figure 1c,d), although there was a considerable amount of amorphous oxide. The octahedral and/or rhombohedral NiO on the NSCT surfaces were approximately 200−300 nm in size.

2.1.2. XRD Pattern Analysis of NSCTs. To analyze the surface oxides, the XRD spectra of the NSCTs were investigated. Figure 2 shows the XRD spectra of NSCT-480 (a,b) and NSCT-600 (c,d). Figure 1a,c shows that amorphous and crystal oxides possibly coexist on the surface. Many regular crystals were observed when the images were magnified 100 000×, indicating that crystal NiO is formed on the NSCTs.29 Compared to those of NSCT-480, the NiO crystals of NSCT-600 were more regular (Figure 1c,d), although there was a considerable amount of amorphous oxide. The octahedral and/or rhombohedral NiO on the NSCT surfaces were approximately 200−300 nm in size.
high OER activity, given the respective. The rhombohedral NiO was assumed to exhibit a 101, 012, 200, and 220 planes of the rhombohedral NiO, peaks at 37, 43, 53, and 76 were determined to correspond to the polycrystalline SnO2, corresponding to the polycrystalline oxide. The featured peaks at 26, 34, 38, and 53 were assigned to the hexa-coordinated polymeric SnO—Sn species. Although the peak at 270 nm was obvious on the surface of the NSCT-600, the strongest adsorption appeared at 220 nm, arising from isolated Sn4+ species in tetrahedral coordination.

From the FT-IR and DRUV—vis spectra of the NSCTs, we found that the high valence of tin on the surface of NSCT-600 exceeded that on NSCT-480.

2.1.4. XPS Analysis of NSCTs. To reveal the intrinsic properties of the NiO—SnO2 p–n junction prepared on the Ti plate, X-ray photoelectron spectroscopy was used to analyze the oxides on the surfaces of the NSCTs. Figure 4 shows that the XPS spectra of Ni, O, Sn, and Ti were slightly different, although the survey XPS spectra were almost identical, indicating that Ni, O, Sn, Ti, and C existed on the surfaces of the NSCTs. Figure 4 shows that both NSCT-480 and NSCT-600 exhibited five peaks. On the surface of NSCT-480, the five peaks corresponding to Ni 2p were observed at 879.9, 872.6, 860.9, 855.4, and 853.7 eV. The main Ni 2p3/2 line at 853.7 eV was assigned to Ni2+. Meanwhile, spin—orbit splitting was observed at 18.9 eV, which was approximately 1.2 eV higher than the value determined by Philip. Analogously, the peaks corresponding to Ni 2p appeared at 879.8, 872.7, 860.7, 855.3, and 853.9 eV on the surface of NSCT-600, and the spin—orbit splitting was at 18.5 eV. The main 2p3/2 peak of NSCT-600 was shifted to higher binding energies by approximately 0.2 eV compared to that of NSCT-480, indicating that Ni2+ and Ni3+ coexist on the surface, implying that part of Ni exhibited a stronger interaction with the OER intermediates due to the redox cycle of Ni2+/Ni3+. Figure 4b shows that the O 1s high-resolution spectra appear to be very similar for both NSCT-480 and NSCT-600, with the two main peaks at 530.6 and 529.2 eV (or 530.6 eV) arising from the Ni—O—H band and Ni—O—Ni(Sn), respectively. The O 1s peak was red-shifted by about 0.1 eV on the NSCT-600 surface, verifying the presence of more metal—oxygen—metal bonds.

This would result in the higher stability of NSCT-600 during the oxygen-evolution reaction in the alkaline solution. The FT-IR data implied that NSCT-600 would have a higher OER activity than that of NSCT-480.

Diffuse reflectance ultraviolet—visible spectroscopy revealed that the band gaps of the prepared NSCT-480 and NSCT-600, according to the Kubelka—Munk function (Ep = 1240/λ), were 3.03 and 3.04 eV, respectively (Figure 3b). The band gap data indicated that the amount of oxygen evolved by NSCTs excited by visible light could be ignored. In the visible region, the absorption bands at approximately 420 nm were attributed to NiO. Simultaneously, the weak adsorption bands at 640—660 nm and the strong absorption bands at 700—750 nm were assigned to the octahedral coordination of Ni3+.

In the UV region, the absorption bands of NSCT-480 were different from those of NSCT-600. The DRUV—vis spectra of NSCT-480 displayed peaks centered at 270 nm, which were associated with hexa-coordinated polymeric SnO—Sn species. Although the peak at 270 nm was obvious on the surface of the NSCT-600, the strongest adsorption appeared at 220 nm, arising from isolated Sn4+ species in tetrahedral coordination.

From the FT-IR and DRUV—vis spectra of the NSCTs, we found that the high valence of tin on the surface of NSCT-600 exceeded that on NSCT-480.

2.1.3. FT-IR and DRUV—vis Investigations of NSCTs. To reveal the surface structures of the oxides, NSCTs were examined using FT-IR and DRUV—vis spectroscopy. Figure 3a shows that the FT-IR spectra of the NSCTs were very different. The strong vibration peaks at 3446.2 cm−1 (O—H) and 1635.4 cm−1 (H—O—H) pointed to a large amount of water molecules being adsorbed onto the surface of NSCT-480. Simultaneously, the absorption peaks at 2354.7 and 1386.7 cm−1 indicated the existence of CO2 originating from air. The main H2O and CO2 adsorption bands at 640—660 nm and the strong absorption bands at 700—750 nm were weaker than those on NSCT-480, corresponding to the peak at 505.3 cm−1, indicating the presence of more metal—oxygen—metal bonds.

This would result in the higher stability of NSCT-600 during the oxygen-evolution reaction in the alkaline solution. The FT-IR data implied that NSCT-600 would have a higher OER activity than that of NSCT-480.

Diffuse reflectance ultraviolet—visible spectroscopy revealed that the band gaps of the prepared NSCT-480 and NSCT-600, according to the Kubelka—Munk function (Ep = 1240/λ), were 3.03 and 3.04 eV, respectively (Figure 3b). The band gap data indicated that the amount of oxygen evolved by NSCTs excited by visible light could be ignored. In the visible region, the absorption bands at approximately 420 nm were attributed to NiO. Simultaneously, the weak adsorption bands at 640—660 nm and the strong absorption bands at 700—750 nm were assigned to the octahedral coordination of Ni3+.

In the UV region, the absorption bands of NSCT-480 were different from those of NSCT-600. The DRUV—vis spectra of NSCT-480 displayed peaks centered at 270 nm, which were associated with hexa-coordinated polymeric SnO—Sn species. Although the peak at 270 nm was obvious on the surface of the NSCT-600, the strongest adsorption appeared at 220 nm, arising from isolated Sn4+ species in tetrahedral coordination.

From the FT-IR and DRUV—vis spectra of the NSCTs, we found that the high valence of tin on the surface of NSCT-600 exceeded that on NSCT-480.
480 and NSCT-600 were tested by CA, i-t, and CP in a 1.0 mol/L NaOH solution under normal pressure and temperature conditions (Figure 6b–d).

Figure 5a,b shows that NSCT-600 had the highest OER activity, exceeding those of NSCT-480, SST, and TiO$_2$/Ti. The OER order was NSCT-600 > NSCT-480 > SST > TiO$_2$/Ti. The Tafel slopes of TiO$_2$/Ti, SST, NSCT-480, and NSCT-600 were 172, 61, 97, and 53 mV/dec, respectively (Figure 5c). The dependence of their Tafel slopes was in good agreement with the LSV curves, except in the case of SST. The lowest Tafel slope was 53 mV/dec, indicating that NSCT-600 had the most active OER. Unfortunately, data for NiO/Ti could not be obtained.

Figure 4. High-resolution XPS spectra of Ni, O, Sn, and Ti on the surface of the NSCTs: (a) Ni, (b) O, (c) Sn, and (d) Ti.

Figure 5. Comparison of LSV, Tafel slope, and CV: (a) LSV of TiO$_2$/Ti and SST, (b) LSV of NSCT-480 and NSCT-600, (c) Tafel slope of TiO$_2$/Ti, SST, NSCT-480, and NSCT-600, (d) CV of NSCT-480 at first, 100th, and 500th cycle, and (e) CV of NSCT-600 at first, 100th, and 500th cycle.
because NiO was rapidly peeled from the Ti plate upon the application of a voltage. To compare the OER activities of NSCT-480 and NSCT-600, the CV curves are shown in Figure 6d,e. The CV curve for NSCT-600 implies that it has a higher current density and lower overpotential than NSCT-480. Meanwhile, on the surface of NSCT-600 (Figure 5e), the oxidation peak was centered at approximately 1.45 V (vs reversible hydrogen electrode (RHE)) and the reduction peak was centered at approximately 1.27 V (vs RHE), corresponding to the redox of Ni2+/Ni3+.45 However, the same phenomenon was not obvious on the surface of NSCT-480 (Figure 5d). The Ni2+/3+ redox phenomena of the NSCTs were consistent with their XPS patterns.

Figure 6a shows the overpotential (\( \eta \)) obtained from the CV curves from the first to the 500th cycle at 1 mA/cm² (NSCT-480 and NSCT-600), 5 mA/cm² (NSCT-480), and 10 mA/cm² (NSCT-600). The \( \eta \) values for NSCT-480 were 644 mV for the first cycle, 500 mV for the 100th cycle, and 517 mV for the 500th cycle at 1 mA/cm², respectively. Similarly, the \( \eta \) values for NSCT-600 were 557 mV for the first cycle, 195 mV for the 100th cycle, and 194 mV for the 500th cycle at 1 mA/cm², while they were 1143 mV for the first cycle, 989 mV for 100th cycle, and 961 mV for 500th cycle at 5 mA/cm², respectively. Although the \( \eta \) values were high when fresh NSCTs were tested, the values fell sharply as the test progressed. The optimal \( \eta \) was only 194 mV at 1 mA/cm², which was superior to that of the NiO films deposited onto clean Ti (\( \eta = 425 \) mV at 1 mA/cm²)46 and Au/Ti (\( \eta = 300 \) mV at 1 mA/cm²).47 This result indicated that the presence of SnO2 could promotes the OER performance of NiO in the p-n heterojunction NiO–SnO2 ceramic materials.

Figure 6b shows the results of the steady-state galvanostatic measurement of the NSCTs in a 1.0 mol/L NaOH solution at a current density of 0.102, 0.204, 0.408, 0.816, and 1.632 mA/cm². Evidently, the NSCTs remained stable even at a high current (1.632 mA/cm²) and applied voltage (2.32 V for the NSCT-480 and 2.12 V for the NSCT-600). Relative to the NSCT-480, the stability of the NSCT-600 decreased slightly with an increase in the applied voltage, although the voltage applied to the NSCT-600 was 0.13–0.29 V lower. However, the lower voltage clearly indicates that the NSCT-600 is more conductive than the NSCT-480.

To further illustrate the OER stability, Figure 6c shows the \( i-t \) curves for NSCTs at 1.5 V in a 1.0 mol/L NaOH solution. Figure 6c shows that the current was very high, reaching 120 mA/cm² on the NSCT-600 once the voltage was applied. However, the current fell with an increase in the reaction time and finally stabilized at 10 mA/cm² after 6000 s. We also found that the current of the NSCT-480 was 90 mA/cm² when 1.5 V was applied. The current decreased from 90 mA/cm² to approximately 50 mA/cm² after 3000 s, but it was not stable. Although the current of the NSCT-600 was approximately 40 mA/cm² lower than that of the NSCT-480, the stability of the NSCT-600 was obviously superior to that of the NSCT-480.

Furthermore, chronopotentiometry at 10 mA/cm² was used to identify the activity and stability of the NSCTs. Figure 6d shows how the voltage changes with an increase in the reaction time. Clearly, the voltages applied to the NSCT-480 and NSCT-600 increased sharply with the increase in the reaction time and, after 25 s, reached 3.10 and 3.20 V, respectively. Subsequently, the applied voltages decreased as the reaction time increased. After 3000 s, the voltage applied to the NSCT-600 was only 1.29 V, which was 1.41 V lower than the voltage applied to the NSCT-480. In other words, the current reached 10 mA/cm² when the overpotential of the NSCT-600 was about 600 mV. This result was consistent with the results of the cyclic voltammetry test. However, to obtain the same current, the NSCT-480 required the application of a 1730 mV overpotential, while 7000 s was necessary to stabilize the oxygen evolution.

The above findings verified that the OER activity and stability of NSCT-600 was better than that of NSCT-480 under a given set of conditions.
2.3. Comparative Analyses of NSCTs Before and After Reaction. To reveal the intrinsic relationship between the OER activity and the morphology and surface oxide structure, NSCTs before and after CV testing were analyzed by SEM, XRD, and XPS.

2.3.1. Comparison of SEM Images Before and After Reaction. Figures S1 and S2 show SEM images of the NSCT-480 and the NSCTS-600 after cyclic voltammetry at 0 cycles, and after the 1st cycle, 100th cycle, and 500th cycle. Figures S1 and S2 also show that the captured SEM images are very different before and after CV measurement. This change was also observed by Yu.45

The surface of the rhombohedral particles became blurred once the voltage was applied to the NSCT-480 (Figure S1, 1st cycle). Meanwhile, to obtain currents of 1 and 5 mA/cm², \( \eta_1 = 644 \text{ mV} \) and \( \eta_5 = 1143 \text{ mV} \) must be applied, respectively (Figure 6a). This data indicated that the main consumer of electrical energy was not the evolution of oxygen but rather the changing of the structures of the surface oxides.45 After 100 cycles, a flowerlike crystal formed on the surface of the NSCT-480 with, at that instant, \( \eta_1 \) and \( \eta_5 \) dropping to 500 and 989 mV, respectively. Although a large amount of rhombohedral crystal oxide particles 200–300 nm in size formed again (Figure S1), the values of \( \eta_1 \) and \( \eta_5 \) did not change significantly after 500 cycles (Figure 6a).

Figure S2 shows that the crystal was transformed once a voltage was applied to the NSCT-600. Relative to the NSCT-480, the morphological change in the NSCT-600 surface oxides was less obvious, and the \( \eta_1 \) value was 87 mV lower after the first cycle, indicating that more electrical energy was being consumed for the evolution of oxygen. Although the morphology of the NSCT-600 exhibited crucial differences after 100 and 500 cycles, the overpotentials were 195 mV (1 mA/cm²) and 622 mV (10 mA/cm²) at the 100th cycle, and 194 mV (1 mA/cm²) and 649 mV (10 mA/cm²) at the 500th cycle. The low overpotentials verified that the OER activity of the NSCT-600 was higher than that of the NSCT-480.

2.3.2. Analyses of XRD Patterns Before and After Reaction. To further investigate the relationship between the OER activity and the surface oxide species, XRD patterns of the NSCTs before and after testing were obtained and analyzed. Figure 7 shows that the peak intensities of the metal oxides (TiO₂, SnO₂, and NiO) changed under the influence of the applied voltage. On the surface of the NSCT-480 (Figure 7a–d), the intensities of TiO₂ at 27°, SnO₂ at 26 and 34°, and NiO at 43 and 65° varied before and after the reaction, indicating that the OER activity and stability were affected by the TiO₂ (110), SnO₂ (110), SnO₂ (101), NiO (012), and NiO (220). Similar to NSCT-480, the intensities of the SnO₂ and NiO on the surface of the NSCT-600 (Figure 7e–h) were found to differ before and after the electrochemical measurements. Especially, the activity and stability increased with the increase in the intensity of the NiO and the decrease in the intensity of the SnO₂ for both the NSCT-480 and NSCT-600, implying that the ratio and crystal face of NiO and SnO₂ in the p–n heterojunction NiO–SnO₂ ceramic materials determined the OER activity and stability. All of the data revealed that the p–n heterojunction NiO–SnO₂ ceramic materials with a special crystal face would be highly active and stable OER electrocatalysts.

2.3.3. Investigations of XPS before and after Reaction. To investigate the relationship between the electrocatalytic activity and the valence state of the oxide species, the NSCTs were subjected to survey and high-resolution XPS spectra examinations before and after the CV test (Figures S3, S4, and S8). Figure S3 shows that there is a large difference in the survey XPS spectra of the NSCTs, although Ni, O, Sn, and Ti all existed before and after the reaction. Figure S4 shows the valence state and difference in Ni, O, Sn, and Ti on the surfaces of NSCT-480 and NSCT-600. The intensities of Ni, O, Sn, and Ti fell sharply after 500 CV cycles, indicating that all of the oxides had partially peeled away from the surfaces of the NSCTs. The valence states of Sn and O changed significantly (Figure S3c). The peaks at 497.4 eV proved that the large amount of Ni容易 was not reduced to NiO in the case of both NSCT-480 and NSCT-600 after 500 CV cycles, proving that the redox of Ni容易/Ni容易 is the key to the OER activity and stability of the p–n heterojunction NiO–SnO₂ ceramic materials. Simultaneously, the red shift in the O 1s binding energy reveals that all of the oxides on the surfaces of the
NSCTs changed as a result of the OER tests (Figures S4b and 8). Figure 8 shows that the O1 s red shift values for NSCT-480 and NSCT-600 after 500 CV cycles were 2.7 and 2.4 eV, respectively. The red shift phenomenon revealed that the adsorption of more water on the surfaces of the NSCTs prevented the OH\(^-\) from generating oxygen.

3. CONCLUSIONS

Two p–n heterojunction NiO–SnO\(_2\) ceramic materials on a Ti plate (NSCTs) were fabricated by a simple layer-by-layer method. SEM, XRD, FT-IR, DRUV–vis, and XPS examinations were used to analyze the morphologies and surface structures of the synthesized NSCTs (NSCT-480 and NSCT-600). SEM images revealed that the NSCTs were composed of amorphous oxides and rhombohedral oxides measuring 200–300 nm. The XRD patterns revealed that NiO, SnO\(_2\), and TiO\(_2\) on the surfaces of the NSCTs were polycrystalline compounds. FT-IR and DRUV–vis measurements verified that both NSCT-480 and NSCT-600 exhibited Ni–O–Sn bonding, while the stronger adsorption of H\(_2\)O and CO\(_2\) by NSCT-480 weakened the oxygen-evolution reaction due to OH\(^-\) in an alkaline solution. High-resolution XPS spectra and CV curves revealed, respectively, that there were Nio–O–Ni(Sn) bonds and Ni\(^{2+/3+}\) redox pairs on the surfaces of the NSCTs. The OER activities and stabilities of the NSCTs were measured by CV, CA, i–t, and CP in a 1.0 mol/L NaOH solution. The overpotential of NSCT-600 was 194 mV at 1 mA/cm\(^2\) in a 1.0 mol/L NaOH solution after 500 cycles, indicating that NSCT-600 had a high OER performance. Moreover, the morphologies and surface structures of NSCT-480 and NSCT-600 after 500 CV cycles were analyzed and compared by SEM, XRD, and XPS. It was found that the ratios of NiO and SnO\(_2\), the redox cycle of Ni\(^{2+}\)/Ni\(^{3+}\), and the crystal faces of NiO and SnO\(_2\) were all key to the OER activities and the stability of the p–n heterojunction NiO–SnO\(_2\) ceramic materials. The results of this study will provide a useful guide for the design and fabrication of p–n heterojunction metal-oxide ceramic electrocatalysts with a high level of OER performance.

4. EXPERIMENTAL SECTION

4.1. Regents and Materials. Ethanol, isobutanol, butanol, ethylene glycol, hydrochloric acid, SnO\(_2\), SnCl\(_2\)·2H\(_2\)O, NaOH, and Ni(NO\(_3\))\(_2\)·6H\(_2\)O were purchased from Adamas Reagent Co., Ltd. These analytical grade chemicals were used without further purification unless stated otherwise.

4.2. Fabrication of p–n Heterojunction NiO–SnO\(_2\) Ceramic on the Ti Plate. A titanium plate (Ti > 99.99%, 1 mm thick, measuring 10 mm × 10 mm with a tail measuring 3 mm × 120 mm) was treated successively by an ultrasonic bath, polishing, and then an oxalic acid bath. The Sb-doped SnO\(_2\)/Ti (SST) was prepared as described in our previous report. Details of the processes are given in the Supporting Information.

Typically, the NSCTs were fabricated on an SST as follows. Ni(NO\(_3\))\(_2\)·6H\(_2\)O (0.1 mmol, 290 mg, containing Ni 6.0 mg) was dissolved in 125 μL of hydrochloric acid (12 mol/L). Subsequently, PEG-800 and ethanol (200 μL, \(V_{\text{PEG}-800}/V_{\text{ethanol}} = 4:6\)) were added to the mixture. Modified acrylate (50 μL) was dropped into the above-mentioned solution to form a film containing a Ni complex, which was taken up on the surface of the SST and then baked for 10 min at 145 °C. This was repeated three times and, after the application of the third film, the precursor was calcined for 1 h at 480 °C to fabricate NSCT-480. NSCT-600, TiO\(_2\)/Ti, and NiO/Ti were prepared using the same process but calcined for 1 h at 600 °C. These calcination temperatures were based on the results of our previous research.

4.3. Physical Characterization. NSCT-480 and NSCT-600 were characterized by scanning electron microscopy (SEM, JEOL7800F), Fourier transform infrared spectroscopy (FT-IR, IRPRESTIGE-21), UV–vis diffuse reflectance spectroscopy (DRUV–vis, HITACHI X-650), X-ray diffraction (XRD, Rigaku RAD), and X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250Xi electron spectrometer). Moreover, the SEM, XRD, and XPS results of the NSCTs before and after the electrocatalytic activity tests were compared to determine the intrinsic effects of the OER activity and stability.

4.4. Electrocatalytic Activity and Stability Tests. The electrocatalytic activities and stabilities of NSCTs were investigated using a three-electrode system in an alkaline solution (70 mL 1.0 mol/L NaOH) at 25 °C using an electrochemical workstation (CHI660E Chenhua). In this test system, NSCTs, a Pt plate, and a reversible hydrogen electrode (RHE, Phychemi Co., Ltd.) were used as the working electrode, counter electrode, and reference electrode, respectively. LSV and CV were determined at a scan speed of 5 mV/s.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c03435.

Preparation of Sb-doped SnO\(_2\)/Ti; SEM images of NSCT-480 before and after reaction; and high-resolution XPS of the Ni, O, Sn, and Ti on the surface of the NSCT-480 (PDF)

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Notes
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