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Surface Engineering of a Nickel Oxide–Nickel Hybrid Nanoarray as a Versatile Catalyst for Both Superior Water and Urea Oxidation

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S Supporting Information

ABSTRACT: Developing efficient and low-cost oxygen evolution reaction (OER) electrodes is a pressing but still challenging task for energy conversion technologies such as water electrolysis, regenerative fuel cells, and rechargeable metal-air batteries. Hence, this study reports that a nickel oxide-nickel hybrid nanoarray on nickel foam (NiO-Ni/NF) could act as a versatile anode for superior water and urea oxidation. Impressively, this anode could attain high current densities of 50 and 100 mA cm⁻² at extremely low overpotentials of 292 and 323 mV for OER, respectively. Besides, this electrode also shows excellent activity for urea oxidation with the need for just 0.28 and 0.36 V (vs SCE) to attain 10 and 100 mA cm⁻² in 1.0 M KOH with 0.33 M urea, respectively. The enhanced oxidation performance should be due to the synergistic effect of NiO and Ni, improved conductivity, and enlarged active surface area.



INTRODUCTION

Nowadays, chronically overcommitted fossil energy not only is leading to an energy shortage but also has brought increasing environmental damage for excess emissions of carbon.¹ Hence, it is imperative to search for noncarbonaceous and renewable succedaneums.² Currently, hydrogen fuel has been regarded as an immense alternative to fossil fuels for its low carbon content and optimal energy density.^{3,4} Water splitting driven by universal clean energy sources like wind, water, and solar power has been regarded as the most promising way to obtain nearly endless pure hydrogen. Water electrolysis is composed of oxygen evolution reaction (OER) and hydrogen evolution reaction.⁵ The voltage required to split water is significantly higher than the thermodynamic value (~1.23 V vs RHE) principally because of the sluggish multistep proton-coupled electron-transfer process associated with OER.6,7 Efficient anode catalysts are thereby demanded to facilitate the kinetics of OER.^{8,9} To date, the state-of-the-art OER catalysts are always recognized as ruthenium and iridium and their metal oxides or complexes.¹⁰ However, their poor chemical stability, scarcity, and high cost badly hinder their extensive practical applications.¹¹ Thus, developing earth-abundant and nonnoble-metal-based efficient OER anodes is urgently demanded.¹²

Transition-metal compounds, because of their abundant reserves and low price, have gradually garnered lots of attention for electrocatalysis.¹³⁻²¹ Among them, nickel (Ni)-based compounds like (oxy)hydroxides, chalcogenides, and phosphides are prominent because of their good catalytic power toward the OER.²²⁻²⁵ It should be noted that, although Nibased (oxy)hydroxides like NiO, Ni(OH)2, NiOOH, NiFe

layered double hydroxide, and NiCo2O4 phases have been largely reported to be able to drive the OER catalysis, their catalytic performances have various restrictions such as skimp active sites and high series resistance.^{9,26} Much effort has been recently devoted to developing Ni-based chalcogenides and phosphides as precatalysts toward the OER because of their high conductivity and intrinsic activity. Our group reported a nickel sulfide microsphere film on Ni foam for enhancing the OER activities.²² Sun's group constructed a nickel selenide nanowire film on Ni foam for superior OER catalysis.²³ Hu's group further reported that a Ni₂P phase could efficiently catalyze the OER.²⁴ Although the performances reflected from the above materials are amazing, regrettably, there are still some flaws with these catalysts; for instance, their fabrication processes are cumbersome with the release of toxic H₂S, H₂Se, or H₃P gases. Considering this, researchers shifted their attention toward how to improve the OER performance of Nibased (oxy)hydroxides and mainly proposed two effective strategies: (i) introducing ion dopants into these (oxy)hydroxides phases to improve the native catalytic activity by altering the electronic structures and providing dual or multiple active sites;²⁷⁻²⁹ (ii) surface engineering active substances onto these (oxy)hydroxides to synergistically improve the overall catalytic performance.^{26,30–33} As the most commonly used surface-engineering approach, electrochemical deposition is time-saving and nontoxic and could be performed under ambient temperature, which makes it an effective method to fabricate hybrid catalysts for water electrolysis.^{31,34}

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In this work, a nickel oxide-nickel hybrid nanoarrays on Ni foam (NiO-Ni/NF) built by a facile electrodeposition method could serve as a high-performance 3D OER catalyst is reported. This electrode shows superior and stable OER catalytic performance with the need of overpotentials of only 292 and 323 mV (vs RHE) to drive 50 and 100 mA cm^{-2} in 1.0 M KOH. Also, considering that another anodic oxidation reaction, the urea oxidation reaction (UOR), which has been recognized as a promising alternative to OER for energy-saving hydrogen evolution. $^{35-37}$ This electrode was further demonstrated to be able to drive superior UOR catalysis with the need of just 0.36 V (vs SCE) to drive 100 mA cm⁻² in 1.0 M KOH with 0.33 M urea. The excellent catalytic OER and UOR performances are mainly due to the synergistic effects and compact contacts among Ni, NiO, and Ni foam, greatly improved ion and electronic transfers, as well as enlarged active surface area.

RESULTS AND DISCUSSION

Intuitively, the changes of the optical characteristics demonstrate the successful conversion of NiO–Ni/NF (Figure S1). Then, considering the overlap of the diffraction peak positions for the electrodeposited Ni and Ni foam, NiO–Ni and NiO nanosheets on carbon cloth (NiO–Ni/CC and NiO/CC) were also synthesized with the identical process to verify the existence of electrodeposited Ni on NiO nanosheets. Figure 1a shows the XRD patterns for (a) NiO–Ni/NF, (b) NiO/NF, (c) NiO–Ni/CC, and (d) NiO/CC, in which the diffraction peaks of Ni (electrodeposited Ni or Ni foam), NiO, and carbon cloth are marked with solid diamonds, solid clubs, and solid hearts, respectively. As can be seen, for NiO–Ni/NF, three diffraction peaks located at 44.5°, 51.8°, and 76.4° accord well



Figure 1. (a) XRD patterns. (b) Low- and (inset) high-resolution SEM images of NiO/NF. (c) Low- and (d) high-resolution SEM images of NiO-Ni/NF. (e) TEM and (f) HRTEM images for NiO-Ni nanosheets scratched from Ni foam.

with the standard pattern of Ni [(111), (200), and (220) planes; JCPDS 04-0850], respectively. The other three weak peaks at 37.2° , 43.3° , and 62.9° are indexed to the (111), (200), and (220) planes of NiO (JCPDS 47-1049). By contrast, the diffraction peak positions of NiO/NF are the same as those for NiO-Ni/NF, while the peak intensities of Ni are lower than those for NiO-Ni/NF, indicating that Ni has likely been deposited on the NiO nanosheets. Moreover, the XRD pattern of NiO–Ni/CC has the characteristic peaks of both NiO and Ni phases, while NiO/CC only has the characteristic peaks of NiO, further confirming the existence of Ni.

Figures S2 and S3 and 1b show the SEM images of bare Ni foam, Ni(OH)₂/NF, and NiO/NF, respectively. As observed, the NiO nanosheets are thin and smooth (Figure 1b), while the NiO-Ni nanosheets turn out to be rough and thick (Figure 1c,d). Apparently, the Ni nanoparticle film adheres to the surface of the NiO nanosheets. Note that the thicknesses of the hybrid nanosheets will change according to the increase of the electrodeposition cycles (Figure S4). After 20 cycles, only a teeny weeny thickness change and infrequent Ni particles could be observed (Figure S4a). After 40 cycles, the NiO nanosheets were fully covered by a thick Ni nanoparticle film (Figure S4c). The distribution of Ni and O elements could be confirmed by EDX spectroscopy and corresponding elemental mapping (Figure S5). The TEM image of NiO-Ni nanosheets scratched from Ni foam further shows a well-defined rough nanosheet morphology (Figure 1e). High-resolution TEM (HRTEM) images (Figure 1f and insets) reveal that this configuration has well-resolved lattice fringes with interplanar distances of about 2.05 and 2.09 Å, which could be, in general, indexed to the (111) and (200) planes of Ni and NiO, respectively. XPS measurements were performed to explore the surface chemical compositions and valence states of NiO-Ni/NF (Figure S6). The survey spectrum (Figure S6a) shows the Ni and O elements on the surface of NiO-Ni/NF. The spectrum of NiO-Ni/NF in the Ni 2p region could be divided into six peaks at 879.4, 873.1, 871.3, 860.9, 855.6, and 853.8 eV, respectively (Figure S6b). The peaks centering at 871.3 and 853.8 eV could be assigned to the characteristic feature of Ni⁰, and the peaks at 873.1 and 855.6 eV correspond to Ni²⁺, indicating the existence of Ni²⁺ and Ni⁰ on the surface.³⁸ The remaining two peaks are the satellites.

An OER test has been performed with a typical threeelectrode cell in 1.0 M KOH. To exclude the distraction of electrolyte solution resistance and study the inherent electrochemical activity of the electrode, ohmic resistance corrections were applied to the initial data.^{39,40} Impressively, NiO-Ni/NF is highly efficient toward the OER, as shown in Figure 2a,b. Figure 2a shows polarization curves of NiO-Ni/NF, NiO/NF, and bare Ni foam on the reversible hydrogen electrode (RHE) scale. The oxidation peak detected at \sim 1.38 V (vs RHE) before the onset potential of the OER could be attributed to the conversion of low-valence Ni to high-valence Ni species.^{31,41-43} Obviously, the oxidation peak of NiO-Ni/NF is much higher than that of NiO/NF (bare Ni foam has no visible oxidation peak). Also, the polarization curve of NiO-Ni/NF increases sharply and has a larger gap compared to the contrasts at higher potentials. In detail, bare Ni foam exhibits inferior OER activity and NiO/NF has a higher current response with the need of overpotentials of 415 and 454 mV to drive the current density of 50 and 100 mA cm⁻², respectively. In sharp contrast, NiO-Ni/NF attains 50 and 100 mA cm⁻² at the extremely low overpotentials of 292 and 323 mV, respectively. It is noted that



Figure 2. (a) Polarization curves of NiO–Ni/NF, NiO/NF, and bare Ni foam at a scan rate of 5 mV s⁻¹. (b) Corresponding Tafel plots. (c) The histogram of a comparison of the overpotentials and Tafel slopes between different electrodes. (d) Nyquist plots of NiO–Ni/NF and NiO/NF in 1.0 M KOH under the influence of an alternating-current voltage of 5 mV. (e) Multicurrent process of NiO–Ni/NF. The current density started at 10 mA cm⁻² and ended at 100 mA cm⁻² with an increment of 10 mA cm⁻² per 500 s (inset: enlarged curves). (f) Chronopotentiometric curve of NiO–Ni/NF with a constant current density of 10 mA cm⁻². The inset shows polarization curves recorded for NiO–Ni/NF before and after long-term OER reaction at a scan rate of 5 mV s⁻¹. All experiments were conducted in 1.0 M KOH.

the OER of NiO–Ni/NF outperforms most of the recently reported superior OER catalysts (Table S1). Besides, the OER performances of Ni(OH)₂–Ni/NF, Ni/NF, and Ni(OH)₂/NF were also tested (Figure S7). All of these electrodes have inferior OER catalytic activities compared with NiO–Ni/NF. Their corresponding cyclic voltammograms were also recorded in this potential window (Figure S8). The anodic peaks of NiO–Ni/NF and NiO/NF in the cyclic voltammograms are similar to that in Figure 2a, and the cathodic peaks could be attributed to the reduction of high-valence Ni species formed during the oxidation sweep.¹⁹

In addition, the optimal experimental data show that, with the increase of the deposition cycles, the catalytic activity of NiO–Ni/NF first goes up and then down, which could be attributed to the fact that too much Ni hinders access of the electrolyte to the active sites (Figure S4d). Figure 2b shows the Tafel plots. The Tafel slope of NiO–Ni/NF attains 101.1 mV dec⁻¹, which outperforms 110.4 mV dec⁻¹ of NiO/NF and 143.4 mV dec⁻¹ of Ni foam. The smaller Tafel slope of NiO– Ni/NF implies more rapid OER kinetics for the electrode.⁴⁵ A more intuitional comparison of the overpotential and Tafel slope among NiO–Ni/NF, NiO/NF, and bare Ni foam could be seen by the form of the histogram (Figure 2c), in which NiO–Ni/NF has the lowest overpotential and smallest Tafel slope compared to other contrasts. The electrochemical impedance spectroscopy (EIS) measurements of NiO–Ni/ NF and NiO/NF show that NiO–Ni/NF has a smaller polarization resistance of 18.99 Ω than NiO/NF (348 Ω), indicating the better electron-transfer rate and OER catalytic performance of NiO–Ni/NF,²⁶ as shown in Figure 2d.

To more accurately reflect the comparison of the intrinsic catalytic performance of NiO–Ni/NF and NiO/NF, the massnormalized activity and activity based on the real surface area (RSA) of the electrodes toward the OER were also recorded. As shown in Figure S9, the mass-normalized OER performances of NiO–Ni/NF (mass loading is 1.8 mg cm⁻²) and NiO/ NF (1.7 mg cm⁻²) need potentials of 391 and 445 mV to attain 50 mA mg⁻¹, respectively. Meanwhile, the RSA of Ni foam was measured according to the method introduced in the Supplementary Method. Obviously, a smaller overpotential of 293 mV is needed for NiO–Ni/NF to attain the RSA-based OER performance of 10 mA cm⁻² than that for NiO/NF. These results indicate that the intrinsic catalytic activity of NiO–Ni/NF is much higher than that of NiO/NF.

The catalytic stability of water-splitting catalysts is also vital for application in industry. Figure 2e exhibits a multistep chronopotentiometric curve obtained in 1.0 M KOH, where the current density increases from 10 to 100 mA cm^{-2} with an increment of 10 mA cm⁻² per 500 s. Intuitively, the potential immediately levels off at 1.475 V (vs SCE) and remains constant for 500 s at 10 mA cm^{-2} , which is similar to the rest of the results until 100 mA cm⁻² is reached. This result indicates the excellent mechanical robustness, conductivity, and mass transportation of NiO-Ni/NF.35 The inset of Figure 2e shows a short response time within 3 s, wherein the potential has homologous variation when the current density changes to another step, further proving the fast mass and electron transfers.^{26,37} The chronopotentiometry curve was collected to verify the long-term OER stability of NiO-Ni/NF (Figure 2f). Obviously, there is almost no loss in potential (vs RHE) after 20 h of reaction at a static current density of 10 mA cm^{-2} . The OER polarization curve exhibits only a negligible positive shift after 20 h electrolysis, revealing the good long-term stability of NiO-Ni/NF working in 1.0 M KOH. Note that the oxidation peak of the LSV curve after reaction is higher than that for the initial one, which could be ascribed to the adequate transformation from Ni²⁺ to Ni³⁺ after long-term OER. The SEM images (Figure S10a,b) for NiO-Ni/NF after the OER test show that the morphology gets completely preserved. The corresponding XPS spectra (Figure S10c,d) show that the intensities of the characteristic peaks at 871.3 and 853.8 eV for Ni⁰ obviously decrease after the OER. Considering the possible interference of Ni⁰ in Ni foam on the XPS spectrum of NiO-Ni/NF after the OER, we further collected the XPS spectra of NiO-Ni/CC before and after OER electrolysis. Apparently, the XPS spectrum of NiO-Ni/CC (Figure S11) after the OER also shows a decrease of the intensities of the characteristic peaks of Ni⁰, demonstrating that a portion of the surface Ni might turn out to be the NiOOH phase that is believed to be part of the real active site for the OER.37

The excellent and stable OER catalytic property of NiO–Ni/ NF could be interpreted as the following four reasons. (1) The growing of high-density and upright NiO–Ni hybrid nanosheets on 3D macroporous Ni foam constitutes multistage topology, which provides better contact between the active sites and electrolyte, as well as sufficient spaces for better diffusion of gas bubbles.^{34,44} (2) The compact contact between Ni foam and NiO–Ni hybrid nanosheets ensures good mechanical adhesion and electron transfer without polymer binders. (3) The aforementioned EIS results shown in Figure 2d indicate that NiO–Ni/NF has better conductivity than NiO/NF. (4) The double-layer capacitances at solid/liquid interfaces of NiO–Ni/NF and NiO/NF were tested to estimate their electrocatalytic active surface areas. As shown in Figure S12, the fitting curves (Figure S12c) are obtained from the cyclic voltammograms (Figure S12a,b). The results show that NiO–Ni/NF and NiO/NF have capacitances of 154.5 and 78.2 mF dec⁻¹, respectively, which implies a larger active surface area and more active sites of NiO–Ni/NF.²⁶

Moreover, except for the OER, we found that this NiO–Ni/ NF also has superior UOR activity. The UOR test was performed in 1.0 M KOH with 0.33 M urea with the same device as that for the OER. Figure 3a shows a comparison of



Figure 3. UOR catalytic properties. (a) LSV curves of NiO–Ni/NF in 1.0 M KOH with and without 0.33 M urea. (b) Polarization curves of NiO–Ni/NF, NiO/NF, and bare Ni foam in 1.0 M KOH with 0.33 M urea (inset: corresponding Tafel plots). (c) Polarization plots for NiO–Ni/NF at different scan rates. The inset shows the data replotted as the current density at different scan rates. (d) Chronoamperometric plot of NiO–Ni/NF at a constant current density of 10 mA cm⁻². The inset shows the multicurrent process at different current densities.

the LSV plots of NiO-Ni/NF in alkali with and without urea. It can be observed that NiO-Ni/NF demands a potential of 0.56 V (vs SCE) to attain 100 mA cm⁻² in 1.0 M KOH without urea. In contrast, this electrode exhibits an obvious enhancement in the OER performance, with the need of just 0.36 V to deliver the same current density in 1.0 M KOH with 0.33 M urea. This result confirms that the UOR has taken place on NiO-Ni/NF and is more energy efficient than the OER. Figure 3b shows the UOR activities of NiO-Ni/NF, NiO/NF, and bare Ni foam, in which Ni foam shows poor activity while NiO/ NF has a higher current response, with the need of 0.39 V to attain 100 mA cm⁻². In contrast, NiO-Ni/NF is much more efficient for the UOR and attains current densities of 10, 100, and 200 mA cm^{-2} at just 0.28, 0.36, and 0.45 V, respectively. The activity surpasses most of newly reported superior UOR electrocatalysts (Table S2). As shown in Figure S13, the increase of the current density of urea oxidation is very rapid with the increase of the potentials, which fully covers the oxidation peak of low-valence Ni species. The reason for the formation of reduction peaks is the same as that in alkali. To

gain further insight into the intrinsic catalytic activity of NiO-Ni/NF and NiO/NF for the UOR, the mass-normalized and RSA-based activity of the electrodes toward the UOR are compared in Figure S14, proving that there is a higher intrinsic catalytic activity for NiO-Ni/NF than for NiO/NF. Tafel plots of the three electrodes are given in the inset of Figure 3b. By contrast, NiO-Ni/NF has a lower Tafel slope of 55 mV dec⁻¹, suggesting faster UOR kinetics for NiO-Ni/NF. The UOR performances of Ni(OH)2-Ni/NF, Ni/NF, and Ni(OH)2/NF were also tested (Figure S15). Apparently, these electrodes also have inferior activities toward the UOR compared with NiO-Ni/NF. Besides, the electrodeposition cycles of Ni were also optimized to study the effect of different contents of NiO/Ni on the UOR performance (Figure S16). A total of 30 cycles were chosen as the optimal electrodeposition condition, which is consistent with the result in the OER.

Further, Figure 3c shows LSV curves acquired at different scan rates in alkali with urea. The negligible changes with an increase of the scan rates from 5 to 50 mV s⁻¹ indicate the efficient charge and mass transport of NiO–Ni/NF.^{44,45} Besides, the stable multistep chronopotentiometric curve (inset in Figure 3d) implies the superior conductivity, mass transport, and mechanical robustness of NiO–Ni/NF for the UOR. The long-term UOR catalytic stability of NiO–Ni/NF was further tested (Figure 3d). Obviously, the potential only shows negligible degradation after 16 h of reaction under a constant current density of 10 mA cm⁻², indicating that this electrode has good long-term UOR catalytic stability in alkali with urea. Therefore, NiO–Ni/NF could be well qualified as an excellent and stable anode for catalyzing UOR.

The superior urea electrolysis performance of NiO–Ni/NF also promises its use as a fascinating 3D electrochemical sensor for urea detection. Figure S17 shows the LSV plots of NiO–Ni/NF and the corresponding calibration curve, which are used to study the electrochemical behaviors of NiO–Ni/NF toward different concentrations of urea.^{18,46} As observed, the current density rises with an increase of the concentrations, and there is a linear relationship between the current density and urea concentration in the range of 0–8 mM.

CONCLUSION

In summary, NiO–Ni/NF has been successfully developed for both superior and stable water and urea oxidation via hydrothermal and subsequent electrochemical deposition processes. NiO–Ni/NF could attain 50 and 100 mA cm⁻² at the low overpotentials of 292 and 323 mV in 1.0 M KOH for the OER. This electrode is also efficient for urea electrolysis and just needs 0.36 V vs SCE to drive 100 mA cm⁻². The superior activity and stability of this electrode, accompanied by this easy and controllable preparation process, provides us with a low-cost and high-performance anode alternative for superior OER and UOR catalysis in future industrial water-splitting devices.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.8b00411.

Supplementary method, optical photographs, SEM images, EDX spectrum and elemental mapping, XPS

spectra, CV and LSV plots, electrochemical data, and Tables S1 and S2 (PDF)

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Notes

The authors declare no competing financial interest.

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