Electrocatalytic Water Splitting through the Ni$_{x}$S$_{y}$ Self-Grown Superstructures Obtained via a Wet Chemical Sulfurization Process

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ABSTRACT: We report water-splitting application of chemically stable self-grown nickel sulfide (Ni$_{x}$S$_{y}$) electrocatalysts of different nanostructures including rods, flakes, buds, petals, etc., synthesized by a hydrothermal method on a three-dimensional Ni foam (NiF) in the presence of different sulfur precursors, e.g., thiourea, sodium thiosulfate, thioacetamide, sodium thiosulfate, thiourea, and sodium sulfide. The S$^{2-}$ ions are produced after decomposition from respective sulfur precursors, which, in general, react with oxidized Ni$^{2+}$ from the NiF at optimized temperatures and pressures, forming the Ni$_{x}$S$_{y}$ superstructures. These Ni$_{x}$S$_{y}$ electrocatalysts are initially screened for their structure, morphology, phase purity, porosity, and binding energy by means of various sophisticated instrumentation technologies. The as-obtained Ni$_{x}$S$_{y}$ electrocatalyst from sodium thiosulfate endows an overpotential of 200 mV. The oxygen evolution overpotential results of Ni$_{x}$S$_{y}$ electrocatalysts are comparable or superior to those reported previously for other self-grown Ni$_{x}$S$_{y}$ superstructure morphologies.

1. INTRODUCTION

The oxygen evolution reaction (OER) for water splitting is a top agenda in electrocatalytic energy storage applications. From the cost and availability points of view, ruthenium oxide and platinum electrode materials are envisaged rarely for OER applications in the past; therefore, the research activities are being focused on developing OER electrode materials, such as Co$_3$S$_4$, NiS, MnS, Bi$_2$S$_3$, CuS, etc. In general, react with oxidized Ni$^{2+}$ from the NiF at optimized temperatures and pressures, forming the Ni$_{x}$S$_{y}$ superstructures. These Ni$_{x}$S$_{y}$ electrocatalysts are initially screened for their structure, morphology, phase purity, porosity, and binding energy by means of various sophisticated instrumentation technologies. The as-obtained Ni$_{x}$S$_{y}$ electrocatalyst from sodium thiosulfate endows an overpotential of 200 mV. The oxygen evolution overpotential results of Ni$_{x}$S$_{y}$ electrocatalysts are comparable or superior to those reported previously for other self-grown Ni$_{x}$S$_{y}$ superstructure morphologies.

2. EXPERIMENTAL SECTION

2.1. Experimental Procedure. The experimental procedure has been reported in detail in our previous work. In brief, NiF in the presence of different sulfur source precursors, i.e., sodium thiosulfate (STS), thiouacetamide (TAA), thiourea (TU), sodium sulfide (SS) in 3, 0.45, 6, and 3 g, respectively, was added sequentially in 50 mL of deionized water as a solvent. The above-prepared sulfurized solutions were poured in a 50 mL capacity stainless steel autoclave and heated at 120 °C for 4 h during the heating treatment, each sulfur precursor dissociated to sulfur ions (S$^{2-}$) (see the detailed chemical reaction in the Supporting Information S1 (SI), which successively could react with nickel ions from NiF, resulting in the formation of the Ni$_{x}$S$_{y}$ superstructure (Figure 1). As-prepared self-grown electrocatalysts were labeled as (a) NiF, for self-grown Ni$_{x}$S$_{y}$ superstructures with different morphologies for electrocatalytic energy storage applications, we report a very convenient and scalable self-grown chemical synthesis approach to obtain the Ni$_{x}$S$_{y}$ superstructure electrodes of different morphologies. After structure, morphology, phase purity, and binding energy measurements, they are envisaged in water-splitting applications where a low OER overpotential and a long-term chemical stability are evidenced.

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(for comparison), (b) Ni$_2$S$_3$–STS, (c) Ni$_2$S$_3$–TAA, (d) Ni$_2$S$_3$–TU, and (e) Ni$_2$S$_3$–SS. All electrocatalyst electrodes were characterized for their structure, surface morphology, and binding energy by means of different characterization tools, as reported previously.\textsuperscript{21}

2.2. OER Confirmation. The OER measurements for the Ni$_2$S$_3$ electrocatalysts were carried out using a three-electrode system (in addition to the use of NiF as a reference) in the presence of a Hg/HgO reference electrode and a platinum counter electrode. Before undertaking experiments, a nitrogen purge was operated for 10 min to normalize the system with respect to external as well as internal oxygen.

2.3. Formulas. Formulas used for estimating the three-electrode electrocatalytic energy parameters are provided in the SI S2.

3. RESULTS AND DISCUSSION

The surface morphologies of the pristine NiF and self-grown Ni$_2$S$_3$ superstructure electrodes are displayed in field emission scanning electron microscopy (FE-SEM) images shown in Figure 2a–e. The surface of NiF obviously changed after hydrothermal sulfurization. We selected a single-branch NiF and self-grown Ni$_2$S$_3$ for analysis (Figure 2a,a1) under low and high magnifications. As can be seen, the FE-SEM image of pristine NiF reflected an uneven, continuous, and smooth surface of Ni oval-shaped grain boundaries and Ni$_2$S$_3$ superstructure electrodes of different morphologies, suggesting a role of precursor solution in the growth process. Figure 2b,b1 confirms the surface of the Ni$_2$S$_3$–STS electrode as volcano-type nanorods of 800 (±100) nm heights. The diameter of these nanorods, separated from one another with open air voids of 200 (±50) nm, dramatically reduced from the top to bottom in the range of 60 (±20) nm. The Ni$_2$S$_3$–TAA electrode surfaces (Figure 2c,c1), consisting of well-grown and uniformly distributed nanoflakes with 5 (±1) nm widths and 100 (±30) nm sized pores, are interlocked into one another. The morphology of Ni$_2$S$_3$–TU (Figure 2d,d1) presents a budlike structure with a diameter of 900 (±300) nm and separation spacing of 1200 (±500) nm (Figure 2e,e1).

In the end, the Ni$_2$S$_3$–SS electrode shows less number of 3 (±2) nm width nanopetals. In a nutshell, after sulfurizing, NiF with different sulfur precursors can be evaluated in different Ni$_2$S$_3$ morphologies, which play an important role in easy electrolyte ion transformation into an interior part of the electrode material when employed in electrochemical energy storage devices.

Furthermore, the presence of the Ni and S elements on the NiF, Ni$_2$S$_3$–STS, Ni$_2$S$_3$–TAA, Ni$_2$S$_3$–TU, and Ni$_2$S$_3$–SS surfaces is confirmed by energy dispersive X-ray (EDX) elemental mapping analysis (Figure S1). From the results obtained, it is confirmed that Ni and S followed a uniform distribution over the NiF surface with an expected atomic percentage; Ni varies from 100 to 43%, whereas S increases from 0 to 40%, suggesting the successful incorporation of S$^2$ into NiF as Ni$_2$S$_3$. With different methods, trial-and-error experiments have been carried out to optimize the condition of the sulfur source, by unoptimizing sulfur precursor weights, with failure results in terms of not-well-sulfurized FE-SEM images shown in Figure S2. This result confirms that the sulfur precursor solution source was allowing NiF to withstand without any breakage during an optimization of the sulfurization process.

The phases present in Ni$_2$S$_3$ were confirmed by X-ray diffraction (XRD), Raman, X-ray photoelectron spectroscopy (XPS), Brunauer–Emmett–Teller (BET), transmission electron microscopy (TEM), and selected area electron diffraction (SEAD) measurements, as given in Figure 3 (A, B, C–E, F–I, J–K, and L, respectively). Ni$_2$S$_3$ was polycrystalline in nature as the XRD patterns showed reflection peaks with moderate intensities (Figure 3A). The two strong intensity peaks (marked as "Δ") at 44.4 and 51.7° were due to (111) and (200) reflections, respectively, of NiF (JCPDS no. 04-0850).\textsuperscript{28} Four new peaks reflected at 18.71° (110), 32.34° (330), 40.74° (021), and 52.01° (401) were attributed to NiS$_2$ (denoted ♦); three peaks at 31.29° (200), 35.93° (210), and 59.85° (321) were attributed to NiS (denoted ♠); and rest five peaks at 21.29° (101), 30.68° (110), 49.04° (113), 50.43° (210), and 55.33° (112) were attributed to Ni$_2$S$_2$ (denoted ♣).
All reflected peaks evidenced the presence of three different phases in NiF after sulfurization.\textsuperscript{17−21} Raman modes were generated in the Ni\textsubscript{x}S\textsubscript{y} superstructure. The reflected Raman peaks were at 142, 246, 298, and 373 cm\textsuperscript{−1} for NiS; 346, 462, 487, and 557 cm\textsuperscript{−1} for NiS\textsubscript{2}; and 185, 280, and 633 cm\textsuperscript{−1} for Ni\textsubscript{3}S\textsubscript{2}.\textsuperscript{21,26−38} A single Raman scattering peak was reflected in NiF due to its metallic character (Figure 3B,a).

The presence of numerous peaks in the broad range of 900−1200 cm\textsuperscript{−1} indicated the existence of sulfate (S\textsuperscript{2−}) ions. An XPS survey scan was carried out to identify the surface valance states; the Ni 2p and S 2p spectra for the Ni\textsubscript{x}S\textsubscript{y}−STS electrode are shown in Figure 3C−E. Occurrence of Ni and S elements was clarified from the survey spectrum. The binding energy positions for Ni 2p\textsubscript{3/2} and 2p\textsubscript{1/2} were at 855 and 874 eV (shown in Figure 3D). A pair of satellite peaks at 860 and 879 eV was also recognized. The peaks at 162.3 and 169 eV in the high-resolution (HR) XPS spectrum for S 2p (Figure 3E) were ascribed to 2p\textsubscript{1/2} and SO\textsubscript{4}\textsuperscript{2−}, which indicate the presence of the S−S band in all of the Ni\textsubscript{x}S\textsubscript{y} electrodes (see Figure S3 for more details for other electrodes). The nitrogen adsorption−desorption isotherm and the pore size distribution (inset) graphs for the Ni\textsubscript{x}S\textsubscript{y}−STS electrode are shown in Figure 3F. The obtained specific surface area and pore size distribution values were 62 m\textsuperscript{2} g\textsuperscript{−1} and 7.4 nm, respectively. The adsorption isotherm in the range of 0.4−0.9 with a slope value ca. 0.4 was allotted to capillary condensation, which is a typical feature of mesoporous materials.\textsuperscript{19,21} The obtained surface area and pore size distribution values for other Ni\textsubscript{x}S\textsubscript{y} electrodes were smaller (38−47 m\textsuperscript{2} g\textsuperscript{−1}) and are given in Figure 3G−I. The HR-TEM images (Figure 3J) of the optimized Ni\textsubscript{x}S\textsubscript{y}−STS electrode, i.e., the formation of volcano-type nanorods, which is well consistent with the FE-SEM images shown in Figure 2b,b1. The HR-TEM scan, as shown in Figure 3K, revealed interplanar lattice fringe separation distances of 0.29 and 0.28 nm for the (111) and (200) planes of NiS\textsubscript{2} and Ni\textsubscript{3}S\textsubscript{2}, respectively. The irregular compact lattice fringes (dotted circle shown in Figure 3K) could be due to an amorphous NiS, suggesting the existence of Ni\textsubscript{3}S\textsubscript{2}, Ni\textsubscript{3}S\textsubscript{2}, and NiS separately in Ni\textsubscript{x}S\textsubscript{y}. Interestingly, the SAED image recorded for the Ni\textsubscript{x}S\textsubscript{y}−STS electrode in Figure 3L showed bright and circular concentric rings, confirming that it is nanocrystalline in nature.

The NiF and in situ grown Ni\textsubscript{x}S\textsubscript{y} electrocatalysts in comparison with RuO\textsubscript{2} were envisaged for OER water catalysis...
activity, as shown in Figure 4A, wherein NiF/RuO₂ showed a very low/high OER activity, whereas NiₓSᵧ−STS after sulfurization showed enhanced electrocatalytic activity at a lower potential of 200 mV relative to the other NiₓSᵧ and RuO₂ electrodes (210, 220, 230, and 138 mV), indicating an improvement in electrocatalytic activity for OER after sulfurization. An oxidation peak noted could be due to the surface reaction of Ni²⁺ with active Ni³⁺ species in NiₓSᵧ. The inset in Figure 4A shows an actual photograph of electrocatalytic OER testing, with marked evolution of oxygen bubbles, which strongly supported that NiₓSᵧ is used for OER activity.

Figure 4B shows the Tafel plots for the corresponding polarization curves, whose slopes provide information that is favorable for OER activity on the surfaces of the NiₓSᵧ electrocatalysts. With an enhanced OER rate, the slope of the Tafel plots is reduced from 165 to 138 mV dec⁻¹ for the NiₓSᵧ electrocatalyst (see detailed information about formulas used for calculation in the Supporting Information S2 (SI)). The different NiₓSᵧ phases, three-dimensional (3D) structures, and high surface areas with a minimum series resistance increased the water splitting rate for better OER activity. The numerical values obtained for the overpotential and Tafel slope of the NiₓSᵧ−STS electrode were in close agreement to those reported earlier.²²−²⁵,²⁴−²⁵ (Figure 4C). Figure S4A shows the Nyquist plots obtained for the self-grown and NiF electrodes. The value for the charge-transfer resistance (in Ω) obtained for NiₓSᵧ−STS was ≈0.40 (±0.10), lower than that for NiₓSᵧ−TAA (≈0.90 (±0.10)), NiₓSᵧ−TU (≈1.40 (±0.20)), NiₓSᵧ−SS (2.10 (±0.10)), and NiF (≈3.15 (±0.10)) electrodes. The series resistance values for the NiF and NiₓSᵧ electrodes were 3.5, 0.5, 1.4, 1.9, and 1.5 Ω, respectively, meaning a smaller series resistance for the NiₓSᵧ−STS electrode compared to that for other electrodes. The cyclability of the NiₓSᵧ−STS electrocatalyst for OER was further examined by successive CV plots for 1000 cycles (Figure S4B and its inset show polarization curves after 1st and 1000th cycles). A small reduction in the OER activity was corroborated from the NiₓSᵧ−STS CV curves after 1000th polarization curves. Considering the excellent OER catalytic ability for the 1000 polarization curves, the FE-SEM images of the NiₓSᵧ−STS electrode (Figure S4C,D) showed a change in morphology from volcano-type nanorods to aggregated nanoflakes with more crystallinity, one of the common practices in electrochemical measurements. The above result and discussion indicates that NiₓSᵧ−STS acts as an excellent catalyst for OER and there are possible reasons (see Figure 4D) that after sulfurization of NiF its surface area increases with more active sites, wherein OH⁻ intercalation and electron transportation at lower potentials become much easier. The XRD and XPS analyses after the stability study are also shown in Figure S5a,b−d. The XRD pattern of the NiₓSᵧ−STS electrode shows a strong peak of Ni metal with a suppressed NiₓSᵧ peak position due to the formation of an amorphous phase, where, as shown in the XPS spectrum, peak positions of Ni and S shifted toward a lower wavelength side with decreased peak intensity; both elements were decreasing the presence in the NiₓSᵧ−STS electrode except the O peak.

4. CONCLUSIONS

Self-grown 3D NiₓSᵧ superstructures comprising NiS, NiS₂, and NiS₃ crystal structures with different morphologies and high surface areas have been successfully prepared using a hydrothermal method. The structural, morphological, and electrochemical properties of NiₓSᵧ confirm an excellent catalysis performance as compared to that of the pristine NiF. On a similar line, efforts for self-growing NiₓSe, NiₓTe, together with MoS₂, Fe (iron), V (vanadate), and their hybrid superstructures with varying morphologies for better and sustainable electrochemical and electrocatalytic energy storage performance are underway.⁴⁶−⁴⁹

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00132.

Possible chemical reaction mechanisms responsible for the hydrothermal formation of NiₓSᵧ, FE-SEM-based EDX mapping, XPS, stability study, electrochemical energy storage performance formulas (PDF)
Electrocatalysis for the Oxygen Evolution Reaction: Recent Developments in Nanoscale Materials on 3D Nickel Foam as Electrocatalysts for Water Splitting. Involving Solution-Phase Deposition.

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Notes

The authors declare no competing financial interest.

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