MoS$_x$@NiO Composite Nanostructures: An Advanced Nonprecious Catalyst for Hydrogen Evolution Reaction in Alkaline Media

Zafar Hussain Ibupoto,* Aneela Tahira, PengYi Tang, Xianjie Liu, Joan Ramon Morante, Mats Fahlman, Jordi Arbiol, Mikhail Vagin, and Alberto Vomiero*

The design of the earth-abundant, nonprecious, efficient, and stable electrocatalysts for efficient hydrogen evolution reaction (HER) in alkaline media is a hot research topic in the field of renewable energies. A heterostructured system composed of MoS$_x$ deposited on NiO nanostructures (MoS$_x$@NiO) as a robust catalyst for water splitting is proposed here. NiO nanosponges are applied as cocatalyst for MoS$_2$ in alkaline media. Both NiO and MoS$_2$@NiO composites are prepared by a hydrothermal method. The NiO nanostructures exhibit sponge-like morphology and are completely covered by the sheet-like MoS$_2$. The NiO and MoS$_2$ exhibit cubic and hexagonal phases, respectively. In the MoS$_x$@NiO composite, the HER experiment in 1 M KOH electrolyte results in a low overpotential (406 mV) to produce 10 mA cm$^{-2}$ current density. The Tafel slope for that case is 43 mV per decade, which is the lowest ever achieved for MoS$_2$-based electrocatalyst in alkaline media. The catalyst is highly stable for at least 13 h, with no decrease in the current density. This simple, cost-effective, and environmentally friendly methodology can pave the way for exploitation of MoS$_x$@NiO composite catalysts not only for water splitting, but also for other applications such as lithium ion batteries, and fuel cells.

1. Introduction

Hydrogen production by cost-effective electrochemical water splitting is one of the most promising approaches to confront the energy crisis and to obtain clean fuels with high energy density. Hydrogen evolution reaction (HER) aims at meeting the stringent criteria for entering the energy market, through fabrication of electrocatalysts guaranteeing highly efficient hydrogen production.$^{[1,2]}$. However, the best-known electrocatalysts for hydrogen production are Pt and Pt derivatives, which hinder the possibility of application of such technology due to their high cost and scarcity.$^{[3,4]}$. Therefore, the development of environmentally friendly, low-cost, and earth-abundant catalysts to replace noble metals is mandatory to realize large-scale electrocatalytic hydrogen production.$^{[5]}$

To obtain efficient water splitting at a practical level, the electrocatalysts for HER must work either in acidic or in alkaline electrolytes at low overpotential.$^{[6]}$. To develop simple and cost-effective functional catalysts for electrochemical water splitting, the latest research directions involve the investigation of Mo-based nanomaterials,$^{[7]}$ including Mo$_2$C,$^{[8–12]}$ MoN,$^{[13]}$ MoS$_2$,$^{[14]}$ and related compounds,$^{[15–17]}$ aiming at competing with Pt in terms of catalytic efficiency in HER. A successful strategy is the deposition of Mo compounds on various conducting substrates with high specific surface area, including carbon nanosheets,$^{[18]}$ and nanotubes,$^{[19,20]}$ which prevent aggregation of the nanocomposites, keeping the effect of the high density of their active sites.
HER performance of Mo compounds is critically dependent on the crystalline planes exposed to the catalytic activity. For example, in MoS$_2$, (10-10) edges are highly catalytically active, while (0001) basal planes are inert. This observation is driving the research on the development of new materials with limited flat surfaces and increased density of edge sites, such as crystalline, amorphous compounds, and hybrid systems. Researchers also reported recently that strain induced by patterned gold nanocones can activate the basal plane of monolayer 2H-MoS$_2$ for HER. However, despite the promising results, Mo compounds are still below the expectations in terms of functional properties, compared to Pt.

In parallel to Mo compounds, other novel electrocatalysts were recently introduced for HER based on earth-abundant metal chalcogenides and other energy-related applications. A successful strategy to boost functional performances is the application of heterostructured nanomaterials; for example, decoration with Ni/NiO nanoparticles of CoSe$_2$ nanobelts (on a stable glassy carbon electrode) demonstrate improved HER, mainly due to the chemical coupling effect of CoSe$_2$ and of the anchored Ni/NiO. Besides this, the fabrication of catalysts for HER typically needs several successive steps, making the development of a functional electrocatalyst with enhanced HER activity in alkaline media for industrial application a very challenging task to date. NiO electrocatalyst exhibits poor HER performance, due to both the low electrical conductivity and the poor catalytic activity.

For these reasons, aiming at increasing the density of active sites and the electrical conductivity, we propose the development of a MoS$_2$@NiO composite nanostructure, targeting the fabrication of a highly stable and efficient electrocatalyst for HER in alkaline media. Herein, we report a new class of heterostructure materials as robust catalyst for HER in 1 M KOH at room temperature. The electrocatalyst is based on a MoS$_2$@NiO composite structure that reveal an efficient HER activity due to synergetic effect between MoS$_2$ and NiO as supporting cocatalyst material. This composite electrode exhibits excellent performance for HER with a Tafel slope (43 mV per decade) comparable to that of commercial Pt/C and compatible with practical applications. Importantly, the presented electrocatalyst is highly stable with negligible loss of potential for almost 10 h under operation. These results can be of importance not only for water splitting but also for other processes and fields of energy sector, in which new electrocatalysts can improve device functionality, like, for instance, in lithium ion batteries, supercapacitors, and fuel cells.

2. Results and Discussion

Figure 1a shows the morphological features of NiO, revealing a porous and flower-like shape. After the deposition of the MoS$_2$ layer (Figure 1b), the composite nanostructures have porous nanoparticle morphology. Scanning electron microscope (SEM)/transmission electron microscopy (TEM) images of pristine MoS$_2$ (Figure S1, Supporting Information) indicate a nanosheet-like morphology.

X-ray diffraction (XRD) analysis (Figure 1) of pure NiO confirms its cubic phase (diffraction pattern well matching the JCPDS card no. 96-101-0382). After MoS$_2$ deposition, aside to the main NiO cubic phase, which remains the main feature of the XRD pattern, the MoS$_2$@NiO composite exhibits reflections compatible with the presence of NiS phase (JCPDS card no. 96-101-0436) hexagonal. The slight shift of the peaks of the NiO cubic phase suggests the distortion of the original crystalline lattice due to a tensile strain induced by the overgrowth of the MoS$_2$ layer. The presence of NiS can be understood by considering the synthetic route to grow the MoS$_2$ layer, which makes use of a sulfur precursor, leading to in situ formation of NiS, as detected by the XRD analysis. No reflections from Mo-based compounds were detected through XRD analysis, suggesting that, most likely, the majority of the MoS$_2$ compounds in the composite are in an almost amorphous form or present very poor long-range order (as will be confirmed by the high-resolution transmission electron microscopy (HRTEM) analysis). The existence of the NiS phase in the composite structure might have small contribution in the HER due to chemical coupling effect.

To probe the chemical composition, X-ray photoelectron spectroscopy (XPS) studies were carried out. Survey scans were used to obtain the elemental composition (see Tables S1–S3 in the Supporting Information for XPS quantitative analysis). In the MoS$_2$@NiO sample, the Mo:S:O:Ni atomic ratio measured from XPS is equal to 26.5:34.0:36.5:3.0. The low Ni concentration is ascribed to the small signal coming from the underlying NiO layer, suggesting a nearly complete coverage of the NiO nanostructures by the MoS$_2$ layer. The high concentration of oxygen (36.5% at.) indicates that Mo is partially oxidized, as indicated by TEM, suggesting that the NiO underlying layer is covered by a mixture of molybdenum sulfides and oxide.

In Figure 1e, the S2p core level spectrum for MoS$_2$@NiO is reported. The MoS$_2$@NiO contains two spin-split doublets (S2p$_{3/2}$ and S2p$_{1/2}$) with a 4:1 ratio. The high intensity S2p$_{3/2}$ peak is situated at ~161.5 eV and the second lower intensity feature is located at ~163.0 eV. The main S2p core level feature for the composite system can be assigned to S$_2$ and the binding energy is consistent with the 1T phase of MoS$_2$. In Figure 1f, the Mo3d core level spectrum for MoS$_2$@NiO is reported. The Mo3d spectrum of the MoS$_2$@NiO sample contains three spin-split doublets (Mo3d$_{5/2}$ and Mo3d$_{3/2}$) with the Mo3d$_{5/2}$ peaks centered at ~230.0 eV (24%), ~232.4 eV (22%). The feature at 228.7 eV can be assigned to MoO and is compatible with the binding energy of the 1T phase of MoS$_2$.

The higher binding energy features are assigned to Mo$^{5+}$ and Mo$^{6+}$, respectively, in good agreement with literature values. As the Mo$^{5+}$ and Mo$^{6+}$ features are not present in stoichiometric MoS$_2$ films, we expect that they originate from MoO$_x$ or MoS$_{x}$O$_y$ regions in the films. For MoS$_2$@NiO, the relative concentration of the oxygen-derived (Mo$^{5+}$, Mo$^{6+}$) components is about 50%, in good agreement with the stoichiometric values previously reported.

The chemical composition, the morphology, and crystalline features were also analyzed via high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) combined with electron energy loss spectroscopy and HRTEM for both the samples (Figure 2). The pure NiO sample (Figure 2a,b) is composed of Ni and O and no other impurity was detected, as shown in the STEM electron energy loss spectroscopy (EELS) composition maps. Furthermore,
HRTEM confirms that the material crystallizes in the cubic NiO phase, [FM3-M]-Space group 225, with lattice parameters of $a = b = c = 0.4179$ nm, and $\alpha = \beta = \gamma = 90^\circ$, as visualized along the [101] direction.

In the MoS$_x$@NiO sample (Figure 2c,d), the presence of Ni, O, Mo, and S was confirmed in the composite. The HRTEM and the corresponding fast Fourier transform (FFT) spectrum indicate that the nanoplates crystallize in the cubic NiO phase, [FM3-M]-Space group 225, with lattice parameters of $a = b = c = 0.4179$ nm, and $\alpha = \beta = \gamma = 90^\circ$ as visualized along the [110] direction. The detailed structure of the NiO/MoS$_x$ interface and the corresponding FFT spectrum indicate that it crystallizes in the hexagonal MoS$_2$ phase, [P63/MMC]-Space group 194, with lattice parameters of $a = b = 0.3165$ nm, $c = 1.2295$ nm, and $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$ as visualized along the [1-21-3] direction. HRTEM analysis identified the presence of several amorphous nanoflakes, which may correspond to the MoS$_x$ compound, in good agreement with XRD analysis presenting no reflections from MoS$_2$ phases.

Overall, the NiO sample is composed of a porous, flower-like layer of cubic NiO phase, with no detected impurities. The composite system has a more complex structure, with the main fraction of the film being composed of cubic NiO (with distorted lattice) and amorphous MoS$_x$. A parasitic NiS phase is present, together with an MoS$_2$ 1T phase at the surface of the MoS$_x$ layer (detected by XPS) and a hexagonal MoS$_2$ phase at the NiO/MoS$_x$ interface (detected by HRTEM).

**Figure 3a** shows the polarization curves obtained through linear sweep voltammetry (LSV) electrochemical mode for the various electrocatalysts: pristine glass carbon electrode (GCE), MoS$_2$, NiO, MoS$_x$@NiO, and benchmark 20% Pt/C at scan rate of 5 mV s$^{-1}$ in 1 m KOH solution saturated with N$_2$ gas. The GCE shows HER activity at higher potential ($\approx 570$ mV vs reversible hydrogen electrode (RHE)), compared to all the other
Figure 2. a) Annular dark field (ADF) STEM image and corresponding EELS chemical composition maps obtained from the red rectangled area in the ADF STEM micrograph. Individual Ni (red), O (green) maps and their composite. b) Left top: low magnification TEM image showing the nanostructure. Right top: the magnified HRTEM image shows the structural details. Left bottom: HRTEM micrograph showing the twin boundary located at the red squared region. The corresponding FFT spectrum indicates that the material crystallizes in the cubic NiO phase. Right bottom: HRTEM image showing the detailed structure of the blue squared region, which is also visualized from the [101] direction, as confirmed by the FFT spectrum. c) ADF STEM image and corresponding EELS chemical composition maps obtained from the red rectangled area for the NiO/MoS$_x$ composite. Individual element maps and their composites are reported. d) NiO/MoS$_x$ system. Left top: low magnification TEM image showing the distribution of the NiO/MoS$_x$ nanocomposite. Middle and right top: HRTEM micrograph showing the structure of the NiO nanoplate. Left bottom: HRTEM image detail of the red squared region and the corresponding FFT spectrum. Right bottom: detailed structure of the interface at the blue squared region and its corresponding FFT spectrum.

Figure 3. a) LSV HER polarization curves in N$_2$ saturated 1 M KOH at 25 °C. b) Calculated Tafel slopes for the different samples.
samples. The nanostructured MoS$_2$ exhibits HER activity still at high potential (≈508 mV vs RHE), which can probably due to the fact that MoS$_2$ tends to agglomerate during HER experiment, resulting in low density of active edges and thus in poor HER performance. The catalytic activity of NiO is also limited and HER activity is reported at high potential (≈535 mV vs RHE). The composite system, instead, exhibits HER activity at low dynamic potential: the MoS$_2$@NiO composite system achieves 10 mA cm$^{-2}$ current density at 406 mV overpotential. This behavior can be assigned to the synergetic effect of the MoS$_2$ nanosheets on the surface of NiO nanostructures, which increases the density of active edges (thanks to MoS$_2$), and the fast charge transfer guaranteed by the NiO nanostructures. The overpotential for the MoS$_2$@NiO electrocatalyst is close or lower than the reported electrocatalysts such CoP/CC (500 mV),$^{[41]}$ N, P-G (700 mV),$^{[42]}$ MoS$_x$ (540 mV),$^{[25]}$ Co-S/FTO (480 mV),$^{[43]}$ and Co-NR carbon nanotubes (CNTs) (450 mV).$^{[44]}$ The overpotential of noble Pt/C catalyst is about 110 mV, of course lower than MoS$_2$@NiO, but still the reported results for a nonprecious and earth-abundant electrocatalyst can be valuable to develop new nanomaterials for water splitting. These results indicate superior performance for the composite system than for the pure NiO and MoS$_2$ catalysts.

Entering into the investigation of the HER process, the HER kinetics can be evaluated from the linear regions of the Tafel plot, through fitting the linear sweep voltammetry (LSV) curves with the Tafel equation (Equation 1):

$$\eta = \log(j) + a$$  

(1)

where $a$ is related to the exchange current density ($j_0$) and $b$ represents the Tafel slope. In alkaline conditions, the HER kinetics most likely takes place via the formation of hydrogen adsorbed intermediates $(H_{ads})$. The formation of $H_{ads}$ involves electron transfer via the discharge of water by following the Volmer step (Equation 2):

$$H_2O + e^- \rightarrow H_{ads} + OH^-$$  

(2)

The next step in HER is either through a second electron transfer (known as Heyrovsky step (Equation 3):

$$H_{ads} + H_2O + e^- \rightarrow H_2 + OH^-$$  

(3)

or by the Tafel step [Eq. (4)]:

$$H_{ads} + H_{ads} \rightarrow H_2$$  

(4)

Generally, a Tafel slope of 120, 40, and 30 mV per decade correspond to the Volmer, Heyrovsky, or Tafel step as the rate-limiting and determining step in the HER kinetics, respectively.$^{[45-47]}$ The Tafel slope of 43 mV per decade suggests that the Heyrovsky step is determining the rate in 1 M KOH for the MoS$_2$@NiO composite nanostructures as shown in Figure 3b. The Tafel slope for the NiO (46 mV per decade) and the pristine MoS$_2$ (44 mV per decade) indicates that these samples also follow the Heyrovsky mechanism, and that the reaction rate is limited by the electrochemical desorption of the hydrogen gas. The Tafel slope for the GCE is 105 mV per decade, in which the rate of reaction is limited by the Volmer step and induces slower HER activity in this sample. The Tafel slope of Pt/C noble catalyst is 30 mV per decade, indicating that the electrochemical reaction is limited by recombination (Tafel step). The values of the Tafel slopes for MoS$_2$@NiO, NiO, and MoS$_2$ (≈40 mV per decade) are relatively low, almost one half of the reported Ni-based and other electrocatalysts in the alkaline media, including NiO/Ni–carbon nanotubes (82 mV per decade),$^{[45]}$ Ni$_3$S$_2$ nanoparticles (97 mV per decade),$^{[46]}$ CoP nanowires on carbon cloth (129 mV per decade),$^{[41]}$ NiCu nanoalloys (116 mV per decade),$^{[49]}$ Ni–Mo/Cu nanowires (107 mV per decade),$^{[50]}$ and electrodeposited Ni nanoparticles (88 mV per decade).$^{[51]}$

By considering the Tafel slope of the electrocatalyst in this study in alkaline media with respect to reported catalysts, we have produced the best-known electrocatalyst (from this point of view) for HER in alkaline media, which is very important for industrial applications. The smaller the Tafel value, the faster is the HER kinetics and the better for hydrogen production.

Most of the studies in the literature on MoS$_2$-based catalysts for HER use Ni foam and other conducting substrates, which somewhat impairs their validity, since the foam itself is catalytically active. In the present study, instead, the use of powders deposited on GCE prevents the problem of the Ni foam, improving the reliability of the results. It is generally accepted that Ni-based electrocatalysts can be a basis for the future generation of efficient catalysts in alkaline media. We demonstrated Ni-based composites with efficiencies close to that of benchmarking Ni-based electrocatalysts.$^{[45]}$ The performance of MoS$_2$@NiO composite is compared with the Mo-based electrocatalysts in alkaline media from the literature in terms of Tafel slope and overpotential as given in Table S4 in the Supporting Information. Our system has the lowest value for the Tafel slope, which indicates the favorable HER kinetics in the MoS$_2$@NiO composite.

To gain additional information about the HER mechanism, we calculated the electrochemical surface area by simple cyclic voltammetry versus Ag/AgCl (Figure 4a–f), from the slope of the linear fit of the average current density versus the scan rate. We obtained almost similar values for NiO, MoS$_2$, and MoS$_2$@NiO, i.e., (1.46 ± 0.02) × 10$^{-4}$ F cm$^{-2}$ for pure MoS$_2$, (1.45E-4 ± 0.03) × 10$^{-4}$ F cm$^{-2}$ for NiO, and (1.47E-4 ± 0.03) × 10$^{-4}$ F cm$^{-2}$ for MoS$_2$@NiO. From these results, we can deduce that no significant increase in surface area is found in the composite catalysts. The improvement in HER activity should come from the synergetic effects between MoS$_2$ and NiO nanostructures in the composite form and not from an increase in specific surface area.

Figure 5a shows the HER polarization curves of the MoS$_2$@NiO sample before and after the stability test. The composite catalyst is highly stable, without any current density loss. We performed the stability test through chronopotentiometry for the MoS$_2$@NiO composite for 13 h. We found a gradual shift in the voltage from 490 to 510 mV to maintain the current density at 10 mA cm$^{-2}$ the first 2 h, and no potential drop was observed after the 2 h transient for the remaining 11 h.

Electrochemical impedance spectroscopy (EIS) was utilized to quantify the surface phenomena and the kinetics of HER on the developed catalysts (Figure 6). NiO showed two orders of magnitude higher values of total capacitance (Figure 6a) visible at low frequencies in comparison with MoS$_2$. Consistently, the capacitance of NiO film (Figure 6b) visible as ordinate value of...
transition toward the saturation was two orders of magnitude higher than for MoS$_2$. These effects illustrate the higher concentration of charge carriers in NiO film in comparison with MoS$_2$. The mutual integration of MoS$_2$ and NiO led to the monotonous transition of electrocapacitive properties between the pristine films.

The presence of two time-resolved processes visible in the Bode plot (e.g., on the spectra of composite film, Figure 6e) was modeled by two resistor-capacitor (RC) elements in the simplest unified equivalent circuit (inset in Figure 6) developed for an electrode covered with a damaged (porous) coating. Since the boundary between the layers is not ideally smooth, due to increased surface roughness of the porous film, a quantitative analysis of the electrode impedance response requires a more complicated, distributed circuit model featuring constant phase elements (CPE) rather than pure capacitors. The equivalent circuit (inset in Figure 6) providing the best fit consists of the solution resistance $R_s$ and two combined R-CPE units (I and II). A single set of parameters has been used to simultaneously fit the real and imaginary parts of the impedance over the frequency range from 1.25 Hz to 50 kHz. A value of the fitting quality parameter $\chi^2$ of $\leq 0.001$ obtained for all spectra indicates a very good fit. The first R-CPE unit showed smaller RC values than the second one illustrating the faster kinetics of the first process. Therefore, the first R-CPE unit might be assigned to fast electronic transport connected with faradaic phenomena.

Figure 4. a–f). Electrochemical surface area estimated by cyclic voltammetry (a,c,e) against Ag/AgCl as reference electrode in 1 m KOH saturated with N$_2$ gas, and linear fit (b,d,f) for pure NiO (a,b), pure MoS$_2$ (c,d), and MoS$_2$@NiO (e,f).
of HER (where \( R_I \) – charge transfer resistance proportional to reversed rate constant of electrode reaction, CPEI – double layer capacitance of GCE at the bottom of pores), while the second R-CPE unit might be assigned to the slower ionic transport (where \( R_{II} \) – resistance of the film established via pores, CPEII – film capacitance).\(^{[3]}\) Consistently with raw signal evaluation, the NiO film showed a 46 times larger value of capacitance (\( \approx 46 \mu \text{F} \)) in comparison with MoS\(_2\) (1 \( \mu \text{F} \)), while the composite film showed an intermediate value (3 \( \mu \text{F} \)). Coherently, the MoS\(_2\) film showed 4 times larger film resistance than NiO, as shown in Figure 6d. The capacitance of double layer established on glassy carbon on the bottom of pores revealed a smaller alteration on different film material (0.8, 4.5, and 0.7 \( \mu \text{F} \) for MoS\(_2\), NiO, and the composite film, respectively) illustrating the minor morphology change at GCE/film interface as shown in Figure 6e. Importantly, the NiO film showed a significantly larger charge transfer resistance (15 \( \Omega \)) in comparison with pristine MoS\(_2\) and the composite films (4.1 \( k\Omega \) and 475 \( \Omega \), respectively) as shown in Figure 6c. This result explains the fastest HER rate on NiO. The composite film revealed a transitional value of HER rate between the two pristine films NiO and MoS\(_2\).

3. Conclusions

In summary, we developed a novel architecture composed of NiO semiconducting nanostructures covered by a MoS\(_2\) layer through the simple excessive sulfurization method, and we tested it for HER in alkaline media. The NiO and MoS\(_2\) in composite structure exhibit cubic and hexagonal crystalline features, respectively. The composite system is purely composed of Ni, O, Mo, and S elements with no other impurity. The nickel sulfides as a possible minor product may possess an electrocatalytic activity for HER. The synthetic strategy is simple and cost effective and can be used at large scale for the production of functional materials. The chemical sulfurization process results in increased density of active sites in the composite catalysts. The hybrid catalyst demonstrated better HER performance (including stability and durability) compared to pristine MoS\(_2\) electrocatalyst, achieving low overpotential for HER, as demonstrated by the extremely low Tafel slope and high current densities, which has never been reported before for MoS\(_2\)-based catalysts in alkaline media. The obtained lowest Tafel slope value (43 mV per decade), the excellent durability and stability are the prominent features of the new nonprecious electrocatalyst and make it a good candidate for precious metal free catalyst in HER. These results can be useful for not only water splitting, but also in a broader range of applications, like for instance oxygen reduction reactions, supercapacitors, lithium ion batteries, gas sensing, and fuel cells.

4. Experimental Section

Synthesis of NiO Nanostructures and their Composites with MoS\(_x\): Nickel chloride hexahydrate, hexamethylenetetramine, ammonium phosphomolybdate hydrate, L-cystein, potassium hydroxide, and 5\% Nafion were purchased from Sigma Aldrich Stockholm Sweden. All chemicals were of analytical grade and used without further purification.

Synthesis of NiO Nanostructures: NiO nanostructures were obtained by two steps. Firstly, nickel hydroxide nanostructures were prepared by mixing 2.37 g of nickel chloride hexahydrate and 1.41 g of hexamethylenetetramine in 100 mL of distilled water. A homogeneous solution was obtained by constant stirring for 30 min. Then growth solution was covered with an aluminum foil and left into preheated electric oven at 95 °C for 5 h. After the completion of growth time, nickel hydroxide nanostructures were obtained by filtration and followed by washing several times with deionized water and dried at room temperature for overnight. In the second step, nickel hydroxide phase was converted into NiO by calcination at 450 °C in air for 3 h.

Synthesis of MoS\(_x@\)NiO Composite Nanostructures: After the growth of Ni oxide nanostructures, the MoS\(_x\) layer was deposited on them. A quantity of 0.3 g of NiO nanomaterial was immersed in the growth solution of 0.175 g ammonium phosphomolybdate hydrate and 0.275 g of L-cystein in 50 mL of distilled water, each in a separate Teflon vessel of capacity of 100 mL. The Teflon vessel was sealed in a stainless-steel autoclave at 200 °C for 20 h. A thick layer of MoS\(_x\) was deposited on nickel oxides, giving the final structure of the composite materials.

Characterization: The morphology of nanostructures was evaluated by JEOL SEM operated at 15 kV. The crystalline structure and phase purity of pristine NiO and MoS\(_x@\)NiO composite nanostructures was investigated by X-ray powder diffraction using a Philips powder diffractometer associated with CuK\(_\alpha\) radiation (\( \lambda = 1.5418\) Å) at...
The XPS experiments were performed using a Scienta ESCA 200 spectrometer in ultrahigh vacuum at a base pressure of $10^{-10}$ mbar with a monochromatic Al (K alpha) X-ray as a source of photons with 1486.6 eV. The XPS experimental methodology was set in such a way so that the full width at half maximum of the clean Au 4f7/2 line was 0.65 eV. All spectra were obtained at a photoelectron takeoff angle of 0° (normal emission). All the samples for HRTEM and STEM were prepared via a mechanical process, as published elsewhere. HRTEM and STEM images were collected by means of a FEI Tecnai F20 field emission gun microscope with a 0.19 nm point-to-point resolution at 200 kV equipped with an embedded Quantum Gatan Image Filter for EELS analyses. The collected images were analyzed by means of Gatan Digital Micrograph software.

Electrolysis of Water in Alkaline Media: All HER experiments were carried on a Solartron analytical potentiostat using a three-electrode cell assembly in 1 M KOH solution saturated with N₂ gas.
The catalyst ink was prepared by 10 mg of each catalyst in 2 mL of distilled water and 100 μL of 5% Nafion and mixture was sonicated in ultrasonic bath for 15 min in order to get a homogenous catalyst ink. A glassy carbon electrode (3 mm in diameter) was applied as working electrode for deposition of 10 μL of catalyst ink by drop casting method and used as working electrode. The modified glassy carbon electrode was dried with flow of N2 gas at room temperature. An Ag/AgCl with saturated KCl as reference electrode and platinum mesh was used as counter electrode, respectively. LSV was employed at the scan rate of 5 mV s⁻¹ for HER characterization in alkaline media.

EIS experiment was performed in the frequency range of 50 kHz to 1.25 Hz with onset potential of 100 mV and an amplitude of 10 mV at the reference. The capacitance double layer was used to estimate active surface area by cyclic voltammetry against Ag/AgCl. The potential versus RHE was calibrated to RHE through Nernst equation.

$$E_{RHE} = E_{Ag/AgCl} + 0.059 \text{pH} + E_{Ag/AgCl}^0$$

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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[1] J. A. Turner, Science 2004, 305, 972.
[2] J. Wang, W. Cui, Q. Liu, Z. Xing, A. M. Asiri, X. Sun, Adv. Mater. 2016, 28, 215.
[3] M. G. Walter, E. L. Warren, J. R. McKone, S. W. Boettcher, Q. Mi, E. A. Santori, N. S. Lewis, Chem. Rev. 2010, 110, 6446.
[4] Y. Zheng, Y. Jiao, Y. Zhu, L. H. Li, Y. Han, Y. Chen, A. Du, M. Jaroniec, S. Z. Qiao, Nat. Commun. 2014, 5, 3783.
[5] V. R. Stamenkovic, B. S. Mun, M. Arenz, K. J. Mayrhofer, C. A. Lucas, G. Wang, P. N. Ross, N. M. Markovic, Nat. Mater. 2007, 6, 241.
[6] E. A. Hernández-Pagán, N. M. Vargas-Barbosoa, T. Wang, Y. Zhao, E. S. Smotkin, T. E. Mallouk, Energy Environ. Sci. 2012, 5, 7582.
[7] J.-S. Li, Y. Wang, C.-H. Liu, S.-L. Li, Y.-G. Wang, L.-Z. Dong, Z.-H. Dai, Y.-F. Li, Y.-Q. Lan, Nat. Commun. 2016, 7, 11204.
[8] H. B. Wu, B. Y. Xia, L. Yu, X.-Y. Yu, X. W. (D) Lou, Nat. Commun. 2015, 6, 6532.
[9] Y. Zhao, K. Kamiya, K. Hashimoto, S. Nakanishi, J. Am. Chem. Soc. 2015, 137, 110.
[10] F.-X. Ma, H. B. Wu, B. Y. Xia, C.-Y. Xu, X. W. (David) Lou, Angew. Chem., Int. Ed. 2015, 54, 15395.
[11] L. Liao, S. Wang, J. Xiao, X. Bian, Y. Zhang, M. D. Scanlon, X. Hu, Y. Tang, B. Liu, H. H. Girault, Energy Environ. Sci. 2014, 7, 387.
[12] D. H. Youn, S. Han, J. Y. Kim, J. Y. Kim, H. Park, S. H. Choi, J. S. Lee, ACS Nano 2014, 8, 5164.
[13] L. Ma, L. R. L. Ting, V. Molinari, C. Giordano, B. S. Yeo, J. Mater. Chem. A 2015, 3, 8361.
[14] H. Wang, C. Tsai, D. Kong, K. Chan, F. Abild-Pedersen, J. K. Nørskov, Y. Cui, Nano Res. 2015, 8, 566.
[15] M.-R. Gao, J.-X. Liang, Y.-R. Zheng, Y.-F. Xu, J. Jiang, Q. Gao, J. Li, S.-H. Yu, Nat. Commun. 2015, 6, 5982.
[16] D. Merki, X. Hu, Energy Environ. Sci. 2011, 4, 3878.
[17] W. Cui, N. Cheng, Q. Liu, C. Ge, A. M. Asiri, X. Sun, ACS Catal. 2014, 4, 2658.
[18] W.-F. Chen, C.-H. Wang, K. Sasaki, N. Marinkovic, W. Xu, J. T. Muckerman, Y. Zhu, R. R. Adzic, Energy Environ. Sci. 2013, 6, 943.
[19] M. Seol, D. H. Youn, J. Y. Kim, J.-W. Jang, M. Choi, J. S. Lee, K. Yong, Adv. Energy Mater. 2014, 4, 1300775.
[20] B. Hinnemann, P. G. Moses, J. Bonde, K. P. Jorgensen, J. H. Nielsen, S. Horch, I. Chorkendorff, J. K. Nørskov, J. Am. Chem. Soc. 2005, 127, 5308.
[21] H. I. Karunadasa, E. Montalvo, Y. Sun, M. Majda, J. R. Long, C. J. Chang, Science 2012, 335, 698.
[22] J. Kibsgaard, Z. Chen, B. N. Reinecke, T. F. Jaramillo, Nat. Mater. 2012, 11, 963.
[23] M. A. Lukowski, A. S. Daniel, F. Meng, A. Forticaux, L. Li, S. Jin, J. Am. Chem. Soc. 2013, 135, 10274.
[24] D. Kong, H. Wang, J. J. Cha, M. Pasta, K. J. Koski, J. Yao, Y. Cui, Nano Lett. 2013, 13, 1341.
[25] D. Merki, S. Fierro, H. Vrubel, X. Hu, Chem. Sci. 2011, 2, 1262.
[26] H. Vrubel, D. Merki, X. Hu, Energy Environ. Sci. 2012, 5, 6136.
[27] J. D. Benck, Z. Chen, L. Y. Kuritzky, A. J. Forman, T. F. Jaramillo, ACS Catal. 2012, 2, 1916.
[28] L. Liao, J. Zhu, X. Bian, L. Zhu, M. D. Scanlon, H. H. Girault, B. Liu, Adv. Funct. Mater. 2013, 23, 5326.
[29] Y. Li, H. Wang, L. Xie, Y. Liang, G. Hong, H. Dai, J. Am. Chem. Soc. 2011, 133, 7296.
[30] Z. Chen, D. Cummins, B. N. Reinecke, E. Clark, M. K. Sunkara, T. F. Jaramillo, Nano Lett. 2011, 11, 4168.
[31] T. Wang, L. Liu, Z. Zhu, P. Papakonstantinou, J. Hu, H. Liu, M. Li, Energy Environ. Sci. 2013, 6, 625.
[32] H. Li, C. Tsai, A. L. Koh, L. Cai, A. W. Contryman, A. H. Fragapane, J. Zhao, H. S. Han, H. C. Manoharan, F. Abild-Pedersen, J. K. Nørskov, X. Zheng Nat. Mater. 2016, 15, 48.
[33] J. Qi, X. Lai, J. Wang, H. Tang, H. Ren, Y. Yang, Q. Jin, L. Zhang, R. Yu, G. Ma, Z. Su, H. Zhao, D. Wang, Chem. Soc. Rev. 2015, 44, 6749.
[34] H. Tang, C. M. Hessel, J. Wang, N. Yang, R. Yu, H. Zhao, D. Wang, Chem. Soc. Rev. 2014, 43, 4281.
[35] X. Lai, J. E. Halpert, D. Wang, Energy Environ. Sci. 2012, 5, 5604.
[36] H. Ren, R. Yu, J. Wang, Q. Jin, M. Yang, D. Mao, D. Kisaúls, H. Zhao, D. Wang, Nano Lett. 2014, 14, 6679.
[37] Y.-F. Xu, M.-R. Gao, Y.-R. Zheng, J. Jiang, S.-H. Yu, Angew. Chem., Int. Ed. 2013, 52, 8546.
[38] D. Voiry, M. Salehi, R. Silva, T. Fujita, M. Chen, T. Asefa, V. B. Shenyov, G. Eda, M. Chhowalla, Nano Lett. 2013, 13, 6222.
[39] X. Yang, W. Fu, W. Liu, J. Hong, Y. Cai, C. Jin, M. Xu, H. Wang, D. Yang, H. Chen, J. Mater. Chem. A 2014, 2, 7727.
[40] H. Huang, L. Chen, C. Liu, X. Liu, S. Fang, W. Liu, Y. Liu, J. Mater. Chem. A 2016, 4, 14577.
[41] J. Tian, Q. Liu, A. M. Asiri, X. Sun, J. Am. Chem. Soc. 2014, 136, 7587.
[42] Y. Zheng, Y. Jiao, L. H. Li, T. Xing, Y. Chen, M. Jaroniec, S. Z. Qiao, ACS Nano 2014, 8, 5290.
[43] Y. Sun, C. Liu, D. C. Grauer, J. Yano, J. R. Long, P. Yang, C. J. Chang, J. Am. Chem. Soc. 2013, 135, 17699.
[44] Y. Sun, X. Huang, A. Goswami, R. Silva, B. R. Sathe, E. Mikmeková, T. Asefa. Angew. Chem., Int. Ed. 2014, 53, 4372.
[45] M. Gong, W. Zhou, M.-C. Tsai, J. Zhou, M. Guan, M.-C. Lin, B. Zhang, Y. Hu, D.-Y. Wang, J. Yang, S. J. Pennycook, B.-J. Hwang, H. Dai, Nat. Commun. 2014, 5, 4695.
[46] Y. F. Xu, M. R. Gao, Y. R. Zheng, J. Jiang, S. H. Yu, Angew. Chem., Int. Ed. 2013, 52, 8546.
[47] E. J. Popczun, J. R. McKone, C. G. Read, A. J. Biacchi, A. M. Wiltrout, N. S. Lewis, R. E. Schaak, J. Am. Chem. Soc. 2013, 135, 9267.
[48] N. Jiang, Q. Tang, M. Sheng, B. You, D.-E. Jiang, Y. Sun, Catal. Sci. Technol. 2016, 6, 1077.
[49] X.-D. He, F. Xu, F. Li, L. Liu, Y. Wang, N. Deng, Y.-W. Zhu, J.-B. He, J. Electroanal. Chem. 2017, 799, 235.
[50] Z. Zhao, J. Huang, Y. Liu, J. Shen, H. Wang, X. Yang, Y. Zhu, C. Li, J. Mater. Chem. A 2017, 5, 4207.
[51] S. Tao, F. Yang, J. Schuch, W. Jaegermann, B. Kaiser, ChemSusChem 2018, 11, 948.
[52] Z. Algharaibeh, P. G. Pickup, Electrochim. Acta 2013, 93, 87.
[53] a) R. D. Armstrong, A. T. A. Jenkins, B. W. Johnson, Corros. Sci. 1995, 37, 1615; b) M. Donoghue, R. Garrett, V. Datta, P. Roberts, T. Aben, Mater. Perform. 2003, 42, 36.
[54] Y. Pan, Y. J. Chen, X. Li, Y. Q. Liu, C. G. Liu, RSC Adv. 2015, 5, 104740.
[55] A. Fontcuberta i Morral, J. Arbiol, J. D. Prades, A. Cirera, J. R. Morante, Adv. Mater. 2007, 19, 1347.