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An efficient bifunctional electrocatalyst based on nickel iron layered double hydroxide functionalized Co₃O₄ core shell structure in alkaline media

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Abstract

Developing a highly active nonprecious and binder free bifunctional electrocatalysts for water splitting is a challenging task. In this study, we used a simple strategy to deposit a nickel iron layered double hydroxide (NiFeLDH) onto cobalt oxide (Co₃O₄) nanowires. The cobalt oxide nanowires are covered with a thin nanosheets of NiFeLDH forming a core shell structure. The Co₃O₄ nanowires are containing the mixed oxidation states of Co²⁺ and Co³⁺ and the surface modification of Co₃O₄ nanowires with NiFeLDH has shown synergetic effects due to the more oxygen defects, catalytic sites, and the enhanced electronic conductivity. Further, the deposition of the NiFeLDH onto Co₃O₄ nanowires demonstrated a bifunctional activity for the water splitting in 1M KOH aqueous solution. From hydrogen evolution reaction (HER), a current density of 10 mA/cm² is achieved at a potential of -0.303 V vs reversible hydrogen electrode (RHE). While for the case of oxygen evolution reaction (OER) a current density of 40 mA/cm² is measured at a potential of 1.49 V vs RHE. Also, this electrocatalyst has shown a considerable long-term stability of 15 h for both the HER and the OER. Importantly, electrochemical impedance spectroscopy has shown that the NiFeLDH integration onto cobalt oxide exhibited around 3 times decrease of charge transfer resistance for both the HER and the OER in comparison with pristine cobalt oxide films, which reveals an excellent electro catalytic activity for both faradaic processes. All these results confirm that the proposed electrocatalyst can be integrated into an efficient water splitting system.

Keywords: Cobalt oxide nanowires, NiFeLDH, water splitting

Electrochemical/photoelectrochemical water splitting is of great potential as a renewable energy alternative, and even for storage devices and other applications including sustainable hydrogen generation, metal air batteries and fuel cells ^[1-5]. To date, the state-of-art catalysts for splitting water are both IrO₂/ RuO₂ and Pt for the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER), respectively ^[1,6]. However, an expensive nature and high scarcity of these precious metal-based catalysts are the big barriers for their large-scale utilization ^[1, 6]. Currently, there are only two commercial water electrolysis such as alkaline and proton exchange membrane (PEM). It is proven that PEM water electrolysis is highly efficient for the hydrogen production, but it uses precious metals like e.g. platinum (Pt) or iridium (Ir)-based catalysts ^[7, 8]. However, low cost alkaline water electrolysis is a promising technology for large-scale hydrogen production, but it is limited by the poor efficiency of electrocatalysts for the hydrogen production ^[9, 10]. Furthermore, alkaline water electrolysis consumes high energy in order to overcome the slow reaction kinetics of OER. Thus, it requires a high cell voltage typically in the range of 1.8 -2.4 V vs RHE that is significantly greater than the thermodynamic value of 1.23 V vs RHE to catalyze the water splitting, and consequently it contributes less than 5% in the industrial hydrogen production ^[10-12]. Thus, high urgency is required for the rational design of efficient non-noble catalysts for the overall water splitting in order to boost up the industrial/commercial applications.

Recently a drastic rise in the design of bifunctional catalysts has been a popular research topic. This is clearly seen from the existing published literature addressing the overall water splitting at a considerable rate in alkaline media using materials such as metal oxides MoO₂, NiCoO₄ ^[13-15], layered double hydroxides (LDH) e.g., NiFe LDHs ^[16], sulfides NiCo₂S₄, MoS₂/Ni₃S₂ ^[17, 18], selenides (e.g. NiSe) ^[19], and phosphides CoP₂/reduced graphene oxide, (Ni₅P₄) ^[20,21]. Surprisingly, many of these published works show a low current density most likely less than 20 mA/cm² and do not describe their low energy conversion efficiency at higher current densities that is of importance for commercial applications. All these reported electrocatalysts are still not optimized, thus they cannot be used for large-scale industrial applications ^[10, 22]. Importantly, the possible difficulty is coming from the integration of both HER and OER catalysts into a single bifunctional catalyst that can operate in same electrolyte. Keeping these challenges in mind, designing a single bifunctional catalyst with enhanced HER and OER activities in the same electrolyte is highly demanded.

Herein, we report a cost-effective strategy for the design of non-noble bifunctional catalysts that comprised on the functionalization of NiFeLDH on Co₃O₄ nanowires for the first time. The hybridization of both materials mitigates their limitations when used separately in water electrolysis. This hybridization produces a highly efficient bifunctional catalyst and gives a current density of 10 mA/cm² at -0.303 V vs RHE in HER and a current density of 40 mA/cm² at 1.49 V vs RHE in OER. Importantly a long-term stability for 15 h is demonstrated by the NiFeLDH on core shell structure.

The distinctive scanning electron microscopy (SEM) images of the NiFe LDH, pristine Co₃O₄, and NiFeLDH functionalized Co₃O₄ nanowires are depicted in Figure 1. Figure 1a shows the pristine NiFeLDH deposited on the Fluorine doped Tin Oxide (FTO), which shows a porous like structure with few hundred nm lateral sides, and all of them are interconnected. As shown in Figure 1b, the pristine Co₃O₄ has nanowires like morphology comprised on the self-assembly of nanoparticles. The length of Co₃O₄ nanowires is a few microns and approximately 50 to 100 nm in diameter. After the electrodeposition of the NiFeLDH on the Co₃O₄ nanowires, the complete surface of the nanowires is covered with NiFeLDH forming a core-shell structure as shown in Figure 1c-d. The NiFeLDH on Co₃O₄ nanowires is comprised on interconnected nanosheets with a thickness of 150 nm to 300 nm.

The elemental composition of pristine Co₃O₄ was investigated by the EDS mapping (not shown here but see the supplementary data Figure S1). The Co and O are uniformly distributed in the nanowire structure and the corresponding EDS spectra revealed the presence of Co and O as main constituents of the nanowire. The Sn element is merged from the FTO substrate in the EDS spectra. The NiFeLDH functionalized Co₃O₄ nanowires confirms the presence of Ni, Fe, Co, and O elements and successfully demonstrated the composite structure as shown in Figure 2. The Ni and Fe elements are homogeneously distributed over the Co₃O₄ nanowire indicating the compatibility of the composite structure and that help in producing the synergetic effect which further facilitated the water splitting.

The powder XRD was used to investigate the phase and purity of the pristine Co₃O₄ and NiFeLDH functionalized Co₃O₄ nanowires as shown in Figure 3. The pristine Co₃O₄ exhibited cubic phase with excellent crystallinity and the diffraction patterns are well matched to the standard JCPDS card no. 96-900-5890. After the functionalization of the NiFeLDH onto the Co₃O₄ nanowires, some of the Co₃O₄ peaks are suppressed and new NiFeLDH peaks appear. The reflection of the

NiFeLDH are in good agreement with the reported standard JCPDS file no. 40–0125. However, the Co_3O_4 patterns are like that of pristine Co_3O_4 and no crystal structure deformation was identified by the XRD measurements.

The chemical composition and the valence states of the elements of the pristine Co_3O_4 and the NiFeLDH functionalized cobalt oxide nanowires were probed by X-ray photoelectron spectroscopy. Figure S2a shows the presence of Co, O as the main elements in the pristine cobalt oxide. For the pristine Co_3O_4 , two major binding energies peaks observed at 795.35 eV and 780.32 eV are assigned to the $\text{Co}2p_{1/2}$ and $\text{Co}2p_{3/2}$ respectively with spin-orbit separation of 15 eV. This separation is corresponding to the Co^{2+} valence state revealing that a part of Co^{3+} is reduced to Co^{2+} with the creation of oxygen defects ^[23] in the structure of the pristine Co_3O_4 (shown in Figure S2b, Figure S2c) where two oxygen peaks were measured for the O 1s region of the pristine cobalt oxide. The peak at a binding energy of 529.59 eV corresponds to the metal-oxygen bonds. However, the peak at 531.35 eV is appearing due to the surface adsorbed hydroxide in on the pristine cobalt oxide nanostructures. The wide scan survey spectrum of NiFeLDH functionalized Co_3O_4 confirms the presence of Ni, Fe, Co and O elements as shown in Figure 4a. In the case of NiFeLDH functionalized Co_3O_4 nanowires, the Co 2p peaks is centered at 784.28 eV and 800.15 eV as shown in Figure 4b and is assigned to the Co^{2+} valence state, suggesting that a part of Co^{3+} ions is reduced to Co^{2+} with the creation of oxygen defects ^[24]. Figure 4c shows three oxygen peaks located at 532.59 eV, 533.79 eV and 534.59 eV which are assigned to the reduction of Co_3O_4 during the electrodeposition of NiFeLDH and the high binding energy peaks are mainly a contribution from surface oxygen vacancy substances ^[25-27]. Moreover, the peak at 534.59 eV in the O 1s region in the sample of NiFeLDH functionalized Co_3O_4 suggests the generation of oxygen defects on the cobalt oxide ^[28, 29]. Figure 4d shows the that Fe 2p peak is almost invisible as XPS is very surface sensitive, Fe could be not at the surface region. Figure 4e shows a high-resolution Ni 2p XPS spectrum indicating binding energies at 859.46 eV and 877.05 eV which are contributions from the $\text{Ni}^{2+} 2p_{3/2}$ and the $\text{Ni}^{2+} 2p_{1/2}$, respectively. These observations are in good agreement with other reported work [30]. Based on the XPS results, it is safe to say that the creation of oxygen vacancies into the Co_3O_4 , enhanced the electronic conductivity due to the presence of various metallic elements such as Co, Ni, and Fe, and the generation of more active sites in the sample of NiFeLDH functionalized Co_3O_4 core shell structure

which equally contribute towards synergetic effect in the composite materials and consequently excellent water splitting is demonstrated.

Figure 5a shows the OER polarization curves of various materials obtained by linear sweep voltammetry in 1M KOH aqueous solution without iR compensation. The OER activity of the bare FTO substrate is negligible whereas the pristine NiFeLDH is showing a slightly increased OER activity but inferior to that of precious material RuO₂. However, the significant increase in the current density at low onset potential is seen for the pristine Co₃O₄ deposited on the FTO substrate. Further, the functionalization of the NiFeLDH on Co₃O₄ nanostructures has shown low onset potential for water oxidation with a considerable current density due to the synergetic effects produced between the NiFeLDH and the Co₃O₄ nanostructured materials. The presence of Ni, Fe and Co in the composite electrode is playing the main role in developing the synergetic effect due to their catalytic activity and consequently enhanced water splitting is found. A current density of 40 mA/cm² is achieved at a potential of 1.49 V vs RHE which is an improvement compared to that of the recently reported OER perovskite based electrocatalysts [31-35, 36-38]. The OER performance of NiFeLDH functionalized Co₃O₄ electrocatalyst is also superior to many of the active cobalt oxide based electrocatalysts [39-41]. Importantly, an obvious redox peak is found at 1.41 V vs RHE in the polarization curve of the NiFeLDH functionalized Co₃O₄ core shell structure. This is mainly coming from the oxidation current of Ni, however in the case of pristine NiFeLDH deposited on the FTO negligible peroxidation peak has been observed, due to the very thin layer of NiFeLDH onto the FTO substrate as shown in Figure 5a.

It is found that the OER mechanism is complicated, but the widely accepted approach of OER mechanism on transition metal oxides was described by Bockris and Otagawa [42] as given below:

Here M represents the active sites associated with the surface of catalyst. The third step (3) is known as the rate determining step during OER.

The Tafel plot was used to understand the kinetics of OER reaction which is extracted from the linear region of the OER polarization curves. The NiFeLDH functionalized Co₃O₄ electrocatalyst exhibited a Tafel slope of 120 mVdec⁻¹ as shown in Figure 5b which is lower in value than many of the reported OER electrocatalysts [43, 44]. However, the RuO₂ exhibited a Tafel slope of 101 mVde⁻¹, the pristine Co₃O₄ showed 136 mVde⁻¹ and the NiFeLDH has 141 mVdec⁻¹. The relatively high values of Tafel slopes are due to the self-resistance of materials and the FTO substrates [45, 46]. The value of Tafel slope for NiFeLDH functionalized Co₃O₄ electrocatalyst is relatively low which ensures the favorable water oxidation kinetics on its surface. This favorable OER kinetics can be attributed to the good chemical compatibility between the NiFeLDH and the Co₃O₄.

Furthermore, to probe the bifunctionality of NiFeLDH functionalized Co₃O₄ core shell structure, HER activity was also measured in 1M KOH at a scan rate of 5 mV/s. The LSV was used to record the HER polarization curves for the different electrodes such as bare FTO, pristine Co₃O₄ and NiFeLDH, NiFeLDH functionalized Co₃O₄ core shell and 20% Pt/C deposited on FTO in 1M KOH as shown in Figure 5c. The HER curves are reported without iR compensation. The HER was found to be excellent as usual for the Pt at the lowest onset potential as shown in Figure 5c. Among the nonprecious catalysts, NiFeLDH functionalized Co₃O₄ electrode has shown superior HER activity and it can achieve a current density of 10 mA/cm² at a potential of -0.303 V vs RHE which is comparable or superior to several recently reported highly active HER electrocatalysts [47-51]. The HER mechanism in 1M KOH is generally involves three steps as follows:

Volmer reaction: $\text{H}_2\text{O} + \text{e}^- \rightarrow \text{H}_{\text{ads}} + \text{OH}^-$: Discharge step (6)

Heyrovsky reaction: $\text{H}_2\text{O} + \text{H}_{\text{ads}} + \text{e}^- \rightarrow \text{H}_2 + \text{OH}^-$: Desorption step (7)

Tafel reaction: $\text{H}_{\text{ads}} + \text{H}_{\text{ads}} \rightarrow \text{H}_2$: Recombination step (8)

The Volmer reaction, Heyrovsky reaction, and Tafel reaction need a Tafel slope value of 120, 40, and 30 mV dec⁻¹ respectively [52-54].

To evaluate the HER rate, the Tafel slopes were obtained from the linear region of the HER polarization curves as shown in Figure 5d. The estimated Tafel slope for the NiFeLDH functionalized Co_3O_4 was 79 mVdec^{-1} and it follows the Volmer–Heyrovsky reaction mechanism predominantly during the HER and the rate determining step is assigned to the desorption step (Heyrovsky reaction). The value of 79 mVdec^{-1} is approximately close to the recently developed cobalt oxide based HER electrocatalysts^[50, 51]. The small Tafel slope value indicates the favorable HER kinetics for the NiFeLDH functionalized Co_3O_4 . Generally, the range of Tafel slope is between $60\text{--}120 \text{ mVdec}^{-1}$ allowing that HER to proceed on the NiFeLDH functionalized Co_3O_4 followed by the Volmer–Heyrovsky mechanism^[51]. Electrochemical impedance spectroscopy was utilized to quantify the surface phenomena and the kinetics of both HER and OER on the developed catalysts (Fig. 6a-c, 6d-e and 6f). The presence of the NiFe-layered double hydroxide (NiFeLDH) onto the FTO glass slide surface led to the visible increase of the ohmic drop illustrating the poor film conductivity. The integration of the NiFeLDH into cobalt oxide yielded both a decrease of the ohmic resistance and an increase of the total capacitance at frequencies of maximum phase angle (Fig. 6a-c). Coherently, the values of the film resistance and capacitance visible as the coordinates of transition point towards the saturation on Y''/ω vs X' plot^[55] were five times smaller and three orders higher for LDH film deposited onto cobalt oxide in comparison with the pristine NiFeLDH. This manifests the enhancement of the LDH conductivity in the conditions of both HER and OER by means of integration into the highly conductive cobalt oxide (Fig. 6b and 6d-e). The quantification of impedance spectra was carried out by an equivalent circuit developed for an electrode with a damaged (porous) coating (Inset in Fig. 6f)^[56] comprising the solution resistance R_s and two combined RC units (I and II). A single set of parameters have been used to simultaneously fit the real and imaginary parts of the impedance over the frequency range from 0.125 Hz to 100 kHz. A value of the fitting quality parameter χ^2 of ≤ 0.001 is obtained for all spectra indicating a very good fit. Since the interfaces are not ideally smooth due to the increased surface roughness of the porous films, an analysis of impedance data required a more complicated, distributed circuit model featuring constant phase element (CPE) rather than pure capacitor in RC unit I. The capacitance C1 calculated for RC unit I was higher for all film-modified electrodes than C2, which motivates the assignment of C1 to the capacitance of electric double layer at the bottom of pore of the film, R1 to charge transfer resistance of faradaic processes,

C2 to film capacitance and R2 to ionic pore resistance ^[57]. Importantly, the NiFeLDH integration onto cobalt oxide showed ca. 3 times decrease of charge transfer resistance for both HER and OER in comparison with pristine cobalt oxide films, which quantifies the electrocatalysis for both faradaic processes. The ionic pore conductivity was also enhanced by the NiFeLDH integration of onto cobalt oxide for HER. Pristine NiFeLDH showed few orders of magnitude higher values of both charge transfer resistance and ionic pore resistance.

For practical applications, the stability is essential parameter to evaluate the figure of merit of the bifunctional electrocatalysts. The stability of NiFeLDH functionalized Co₃O₄ for OER was investigated at a fixed current density of 40 mA/cm² using chronopotentiometry as shown in Figure 7a. The OER stability indicated a stable response and negligible loss of potential with time that suggests the newly designed binder free electrode can be used for relatively long-term applications. Also, chronopotentiometry was also used to measure the potential drop with time at a fixed current density of 10 mA/cm² on the NiFeLDH functionalized Co₃O₄ for HER as shown in Figure 7b. It shows that the electrocatalyst is highly stable for 15 h which ensured its long-term applicability. There was a negligible loss of potential with time. This reveals the fact that the presented electrocatalyst has ability to maintain the current density almost at same potential and works very well for both Faradic processes. The bifunctional performance of the NiFeLDH functionalized cobalt oxide core shell structure is compared with the recently reported electrocatalyst as given Table S1 and Table S2. The activity of proposed electrocatalyst is superior to many of the efficient catalysts based on cobalt or other materials in terms of onset potential.

In summary, a bifunctional and binder free electrocatalyst based on NiFeLDH functionalized Co₃O₄ core shell structure for the water splitting is designed. The water splitting is highly enhanced by the surface modification of the Co₃O₄ nanowires with NiFeLDH which generated synergetic effects due to the more active sites, oxygen vacancies in Co₃O₄ and a good compatibility between the two materials. The binder free electrocatalyst exhibits excellent HER and OER activity in a 1M KOH alkaline media. A current density of 10 mA/cm² is achieved at a potential of -0.303V vs RHE in HER and a current density of 40 mA/cm² is measured at a potential of 1.49 V vs RHE in the case of OER, these are the significantly low onset potentials for the cobalt based electrocatalysts when considering the bifunctional activity. Importantly,

the EIS has shown that the NiFeLDH integration onto cobalt oxide possessed ca. 3 times decrease of the charge transfer resistance for both HER and OER in comparison with the pristine cobalt oxide films, which confirms a favorable electrocatalysis for both faradaic processes. These findings indicate that the developed bifunctional electrocatalyst can be integrated into efficient water splitting system.

Experimental Section

Cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), ferric nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), urea ($\text{CO}(\text{NH}_2)_2$), potassium hydroxide (KOH), fluorine doped tin oxide (FTO) glass substrate, methanol (CH_3OH), ethanol ($\text{C}_2\text{H}_5\text{OH}$), RuO_2 and 20% Pt/C were of analytical grade and purchased from Sigma Aldrich Stockholm, Sweden. All of them were used as received. Prior to the deposition of the Co_3O_4 on FTO glass substrate, the FTO substrates were sonicated in methanol for 30 minutes and washed several times with the deionized water. They were dried with blowing air at room temperature. A seed solution of cobalt oxide was prepared in alkaline solution of ethanol using 0.1M cobalt chloride hexahydrate and 0.1M KOH. The seed solution was stirred for 2 hours at 65 °C. Then a thin layer of cobalt oxide nanoparticles was spin coated on a cleaned FTO glass substrate then annealed at 130 °C for 20 minutes. The annealing was performed to confirm the firm binding of the cobalt oxide nanoparticles on the FTO substrates. The precursor solution was prepared by mixing 0.1M cobalt chloride hexahydrate and 0.1M urea in 100 mL of the deionized water. Then, the seed layer coated FTO substrates were dipped with downward facets into the growth solution and covered by aluminum foil. Then a beaker containing the FTO glass substrates into the growth solution was kept at 98 °C for 6 hours. After the completion of the growth, the oven was switched off and cooled naturally at room temperature. Then the nanostructured deposited on the FTO substrates were taken out, washed with the deionized water and dried at room temperature. The hydroxide phase of cobalt was converted into cobalt oxide via thermal annealing at 500 °C for 4 hours. The functionalization of the layered double hydroxide NiFeLDH on the cobalt oxide nanostructures was carried out by electrodeposition. The precursor solution was prepared by mixing equimolar nickel nitrate hexahydrate and ferric nitrate nonahydrate in 50 mL of the deionized water. The electrodeposition was performed at -1.0 volts versus silver-silver chloride electrode for 10 minutes. Similarly, pristine NiFeLDH

was deposited on FTO substrate. Afterwards, the morphology of the nanostructured materials deposited on the FTO substrates was explored by high resolution scanning electron microscopy (Hitachi model H-800) at an accelerating voltage of 3.0 KeV. The energy dispersive spectroscopy was used to quantify the presence of elements in the composition of samples. The crystalline structure and purity of the nanostructured materials was evaluated by the Philips powder X-ray diffraction technique connected to CuK α radiation ($\lambda = 1.5418 \text{ \AA}$) source at a generator voltage of 45 kV and a current of 45 mA. X-ray photoelectron spectroscopy was used to confirm the results of the energy dispersive spectroscopy and to confirm the oxidation states of the elements within the structure of the nanostructured materials. X-ray photoelectron spectroscopy (XPS) experiments were performed in 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 experiment was carried out through the full width at half maximum of the clean Au 4f7/2 line was 0.65 eV. The XPS spectra were recorded at a photoelectron takeoff angle of 0° (normal emission).

The electrochemical experiments were carried out using three electrode cell configurations in 1M KOH. A silver-silver chloride (Ag-AgCl) was used as reference electrode, a platinum wire as a counter electrode and 0.5 cm^2 of bare FTO and the nanostructured modified FTO electrode was used as working electrode. The noble 20% Pt/C catalyst ink was prepared by dispersing 10 mg in 2.5 mL of deionized water and 0.5 mL of 5% Nafion. Then catalyst ink was deposited on the FTO substrate by drop casting method. The solution of the 1M KOH was saturated with nitrogen gas for 15 minutes then, the electrochemical measurements were performed. First 10 cyclic voltammetry runs at 5 mV/s were measured in order to stabilize the electrode, then linear sweep voltammetry at a scan rate of 5 mV/s was used to investigate the water splitting activity in 1M KOH. Chronopotentiometry was used to measure the stability of the bifunctional catalysts. While electrochemical impedance spectroscopy was used to understand the kinetics of the bifunctional catalyst for the water splitting in a frequency range of 100 kHz to 0.1 Hz at an amplitude of 5 mV with an onset potentials of 1.47 V vs RHE (reversible hydrogen electrode) for OER and -0.3V vs RHE for HER in 1M KOH.

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Figure Captions

Figure 1: SEM Images, **1a.** pure NiFeLDH, **1b.** pure Co_3O_4 , **1c-d.** NiFeLDH functionalized Co_3O_4 nanowires

Figure 2: **2a.** EDS mapping of NiFeLDH functionalized Co_3O_4 nanowires, **2b** EDS spectrum of NiFeLDH functionalized Co_3O_4 nanowires

Figure 3: XRD spectra **3a.** pure Co_3O_4 , **3b.** NiFeLDH functionalized Co_3O_4 nanowires

Figure 4: **4a.** XPS survey spectrum of NiFeLDH functionalized Co_3O_4 , **4b.** Co 2p XPS spectra of Co_3O_4 functionalized with NiFeLDH, **4c.** O 1s of Co_3O_4 , **4d.** Fe 2p in the NiFe LDH, **4e.** high-resolution XPS of Ni 2p of NiFeLDH functionalized Co_3O_4 .

Figure 5: **5a.** LSV OER polarization curves various electrodes, bare FTO, RuO_2 , pure NiFeLDH, pure Co_3O_4 , NiFeLDH functionalized Co_3O_4 nanowires at scan rate of 5 mV/s in 1M KOH solution, **5b.** the corresponding Tafel slopes from OER polarization curves for different electrocatalysts, **5c.** LSVHER polarization curves various electrodes, bare FTO, pure NiFeLDH, pure Co_3O_4 , NiFeLDH functionalized Co_3O_4 nanowires, 20% Pt/C at scan rate of 5 mV/s in 1M KOH solution **5d.** the corresponding Tafel slopes from HER polarization curves for different the electrocatalysts

Figure 6: **6a-c.** The effect of film composition on total capacitance. The dependencies of the total capacitance calculated from impedance spectra acquired on pristine (cobalt oxide and LDH as black and blue, respectively) and a composite film-modified electrodes (red) on the frequency (A) and on real part of impedance (B and C; onset potential of HER (-0.303 V vs RHE), 10 mV amplitude, 1M KOH, **6 d.e.** The effect of film composition on total capacitance. The dependencies of the total capacitance calculated from impedance spectra acquired on pristine (cobalt oxide and LDH as black and blue, respectively) and a composite film-modified electrodes (red) on the frequency (A) and on real part of impedance (B and C; onset potential of OER (1.47 V vs RHE),

10 mV amplitude, 1M KOH, **6f**. Impedance spectra acquired on pristine and LDH-modified cobalt oxide films (black and red, respectively); solid lines – results of the fitting with equivalent circuit (Inset); onset potential of HER (-0.303 V vs RHE), 10 mV amplitude, 1M KOH.

Figure 7: 7a. The chronopotentiometric OER stability of NiFeLDH functionalized Co_3O_4 nanowires for 15 h in 1M KOH, **7b.** The chronopotentiometric HER stability of NiFeLDH functionalized Co_3O_4 nanowires for 15 h in 1M KOH

Figure 1:

Figure 2:

Figure 3:

Figure 4:

Figure 5:

Figure 6:

Figure 7:

Supplementary data

An efficient bifunctional electrocatalyst based on nickel iron layered double hydroxide functionalized Co₃O₄ core shell structure in alkaline media

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S1. EDS mapping for the elemental distribution in pristine Co_3O_4

S2. a. wide scan survey spectra of pristine Co_3O_4 , **b.** Co 2p XPS spectra of pristine Co_3O_4 , **c.** O 1s for pristine Co_3O_4

Table S1 Comparison of OER activities of the NiFeLDH functionalized Co₃O₄ core shell structure with efficient previously reported electrocatalysts in 1M KOH

Catalyst	Tafel slope	Overpotential @ 10 mA/cm ²	Reference
CoCo LDH	59	393	1
CoOx@CN		~385	2
Co-P films	47	345	3
MnCo ₂ Ox	84	> 410	4
Co ₃ O ₄ /N-rmGO	67	310	5
NiCoOx		420	6
N-G-CoO	71	340	7
NixCo _{3-x} O	64	370	8
NiFe LDH-NS @ DG10 hybrid Free-Standing	52	210	9
Exfoliated NiFe LDHs	40	300	10
NiFe LDH/NF	52.8	224	11
NiFe LDH/NF		240	12
Co ₉ S ₈ /CNS/CNT	48	267	13
FeCoW alloy		232	14
Co ₃ O ₄	84	290	15
N-Co ₃ O ₄	59	310	16
RuO ₂		366	17
IrO ₂ /NF	46	285	18
Co ₃ O ₄ hollow polyhedrons		536	19
Co (OH) ₂ @g-C ₃ N ₄ -5		320	20
CoP@PNC		330	21
SOA-Co ₄ N NW/CC		257	22
CoP ₃ NSs/CC		291	23
CoNPs@C		270	24
NiFeLDH/Co ₃ O ₄ NWs	120	1.49 V vs RHE @ 40 mA/cm ²	This work

Table S2 Comparison of HER activities of the NiFeLDH functionalized Co₃O₄ core shell structure with efficient previously reported electrocatalysts in 1M KOH

Catalyst	Tafel slope	Overpotential @ 10 mA/cm ²	References
CoP/CC, 500	129	500	25
N, P-G	145	700	26
MoS _x		540	27
Co-S/FTO		480	28
Co-NRCNTs		450	29
Co-N-C		270	30
CoO _x @CN		235	31
Ni ₃ FeN-NPs		238	32
Ni ₂ P on Ni foam		221	33
NiFeLDH/Co ₃ O ₄ NWs	79	-303 mV vs RHE @ 10 mA/cm ²	This work

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