Porous-Structured Three-Dimensional Iron Phosphides Nanosheets for Enhanced Oxygen Evolution Reaction

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Abstract: A rational designing nanostructured Earth-abundant and non-precious electrocatalysts for promoting an anodic oxygen evolution reaction (OER) is crucial for cutting-edge energy conversion and storage fields. Herein, we demonstrate a porous structured three-dimensional (3-D) FeP nanosheets on NiO modified Ni electrode (PS-3D-FeP@NiO|Ni) using of a facile and two-step electrodeposition strategy that exhibits enhanced OER under alkaline electrolyte. The as-developed porous-structured 3-D FeP nanosheets on NiO modified Ni electrode exhibits the best OER catalytic activity in relations of low onset potential ($\eta_{\text{onset}}$) of ~1.37 V (vs. RHE), small overpotential ($\eta$) of ~0.17 V to produce the current densities of 10 mA cm$^{-2}$, lower Tafel slope value of ~40.0 mV/dec, higher turnover frequency (TOF) of 0.435 s$^{-1}$, and long-term stability when compared to other CoP@NiO|Ni, NiP@NiO|Ni, CuP@NiO|Ni, NiP|NF (nickel foam), and commercial IrO$_2$|Ni electrodes established in this study. The anodic current density is calculated at the potential of ~1.80 V to be ~580, ~365, ~145, ~185, ~516, and 310 mA cm$^{-2}$ for PS-3D-FeP@NiO|Ni, CoP@NiO|Ni, NiP@NiO|Ni, CuP@NiO|Ni, FeP|NF electrodes, respectively. The porous structured 3-D FeP nanosheets on NiO modified Ni electrode demonstrated a highest current density of ~580 mA cm$^{-2}$ at ~1.80 V in comparison to other electrodes employed in the current investigation. The outperforming OER activity of PS-3D-FeP@NiO|Ni is majorly associated to its porous-structured 3-D sheet-like morphology, large amount of electrochemical active surface area, high electrical conductance characteristics and self-activated/supported active sites, facilitating the catalytic properties. The surface morphology, crystalline structure, chemical composition, and distribution of Fe, P and O elements have not been altered significantly after had a long-term OER test. These experimental results reveal that further optimization of porous structured 3D FeP nanomaterials is highly anticipated for practical water electrolysis systems.

Keywords: transition metal-phosphides; iron phosphides; electrochemical deposition; oxygen evolution reaction; water electrolysis

1. Introduction

Growing concerns with the energy problem and environmental pollution have prompted researchers to look into alternative energy sources to traditional energy sources [1,2]. Water electrolysis is considered as an emergent electrochemical technology for converting energy to generate a non-toxic and sustainable chemical fuel of hydrogen (H$_2$) [3–5]. Electrochemical water electrolysis is a highly demanding reaction, and ground-breaking advances are highly necessary to greatly improve the overall efficiency through rational design and advancement of catalysts for hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) [6,7]. Particularly, the electrochemical water oxidation is a critical for electrochemical energy conversion and storage applications [8,9].

As a result, considerable efforts have been made over the last several decades to design an emergent OER catalyst that will facilitate electrode kinetics and its stability in acidic as well as alkaline medium. Typically, the low availability in earth-crust and higher...
price of the state-of-the-art materials like Pt, IrO$_2$, and RuO$_2$ limit its practicability [10–12]. Non-noble metal based catalytic materials such as transition metal phosphides [13,14], sulfides [15,16], hydroxides [17,18], and non-metallic catalysts, are currently being investigated for improving OER [19,20]. The NiO-based catalysts have been employed for various electrochemical energy conversion reactions with low overpotential and high catalytic current densities [21–23]. Recently, Bu and co-workers reviewed the recent progress of nickel–iron-based electrocatalysts such as layered hydroxides, metal-organic frameworks, oxysulfides, alloys, etc., for improved OER under alkaline electrolytes [24]. Transition metal phosphides (TMP) newly sparked a lot of interest in electrocatalytic OER due to the fact of their low electrical resistivity, high catalytic activity, and ever-lasting stability [25,26]. TMPs have been prepared using a variety of processes, including the solvothermal approach [27], solid-state reduction [28], gas–solid reaction [29], and electrodeposition [30].

For instance, Liu et al. recently reported the fabrication of a FeP coated CeO$_2$ electrocatalyst (FeP@CeO$_2$) by using electrochemical deposition and high-temperature phosphorylation in which the electrode materials delivered the OER overpotential of ~0.24 V at a current density of 100.0 mA cm$^{-2}$ and a Tafel slope of ~39.1 mV dec$^{-1}$ [31]. Huang and co-workers prepared a Ni$_{0.75}$Fe$_{0.25}$-P/PO$_3$@f-CNT catalyst through a two-stage method using a liquid-phase decoration and gaseous phosphorization approach that exhibited OER overpotential of ~0.23 V at 10 mA cm$^{-2}$ and Tafel slope of ~45.5 mV dec$^{-1}$. It is reported that Fe oxide motifs at the edge, corner, or defect locations of Fe oxy-hydroxide, exhibit electrophilicity to mediate the water oxidation reaction. Furthermore, recent studies have discovered that transition-metal phosphide have stronger OER activity than other phosphides [32]. However, TMP derived electrocatalysts still present relatively lower OER catalytic performance when compared to state-of-the-art electrocatalysts. Therefore, considerable efforts to enhance the inherent OER catalytic activity improve the conductivity and optimize the mass-transport characteristics may be executed [33]. Due to the adaptability and extreme prominence, the electrodeposition of TMP has extended devotion on spanning the central nanoscale materials to practical systems and capability to control the structure and electrochemical characteristic relations via amendment of electrochemical parameters [34]. On the other hand, it is worth emphasizing that the choice of electrode substrate is an important aspect in increasing OER performance and gaining fresh insights for handling industrial-scale challenges. As a result, the design and development of inexpensive, exceedingly active, and simple-to-fabricate OER electrode for water electrolysis is a key challenge.

Herein, we report a cost-effective and highly active OER catalyst that fabricates using a facile two-step strategy of porous-structured three-dimensional (3-D) FeP nanosheets on NiO modified Ni electrode (PS-3D-FeP@NiO|Ni) for the first time. The resultant PS-3D-FeP@NiO|Ni electrode delivered outperforming electrocatalytic OER activity under alkaline electrolyte. Specifically, the PS-3D-FeP@NiO|Ni electrode exhibited low onset potential (~1.37 V (vs. RHE)), small overpotential ($\eta$) (~0.17 V @ 10.0 mA cm$^{-2}$), small Tafel slope (~40.0 mV dec$^{-1}$), high turn-over frequency (TOF) (0.435 s$^{-1}$), and long-term stability in comparison with the other electrodes examined in the present study and commercial IrO$_2$|Ni electrodes.

2. Experimental Section
2.1. Materials

Cobalt (II) nitrate hexahydrate (Co(NO$_3$)$_2$.6H$_2$O), ferric chloride anhydrous (FeCl$_3$), copper sulphate (CuSO$_4$), and nickel (II) nitrate hexahydrate (Ni(NO$_3$)$_2$.6H$_2$O) were received from Sigma-Aldrich. Nitric acid (HNO$_3$) and sodium dihydrogen phosphate (NaH$_2$PO$_4$) were received from Alfa-Aesar. The potassium hydroxide (KOH) and commercially available IrO$_2$ catalysts were received from Sigma-Aldrich. All analytical-grade reagents were employed exactly deprived of any additional refinement. All of the solutions in this investigation were made with pure water collected from the ultra-pure deionized water purification system.
2.2. Fabrication of PS-3D-FeP@NiO Nanostructured Electrode

The nickel electrode initially was sonicated for 10 min in a 3.0 M HCl solution to remove any NiOx deposit on the surface, and then completely eroded by water and ethanol before drying in the air. The porous-structured three-dimensional (3-D) FeP nanosheets on NiO modified Ni electrode (PS-3D-FeP@NiO|Ni) was fabricated using a two-step approach. First, nickel electrode was dipped in a 0.1 M nitric acid solution for 1 h to form the rough nickel oxide surface [35,36]. The nickel oxide layer was formed on the surface of Ni electrode via natural formation of the passivation or oxide thin layer when an adequate local concentration was achieved [37]. The formed oxide on nickel surface led a rough surface and created more active oxides, which led to the establishment of a hetero-interface. This may influence the growth of 3D FeP sheets as well as the influence the activity of the catalysts. However, the formed nickel oxide may not dissolve under acidic solution as there is a simultaneous deposition of Fe and P on the surface of NiO|Ni electrode. Second, the resultant NiO modified Ni electrode was dipped in the electrolyte solution containing 0.1 M FeCl₃ + 0.075 M sodium dihydrogen phosphate + 0.1 M nitric acid and applied constant potential of 0.9 V (vs. RHE) for 40 min using a potentiostatic approach [38]. In the typical electrodeposition process (Scheme 1), FeCl₃ was used as the Fe³⁺ source, sodium dihydrogen phosphate was employed as the phosphate source, and nitric acid was utilized as the electrolyte. The transition metal cations of Fe³⁺ and hypophosphite anions in the electrolyte solution were reduced into their corresponding Fe atom forms by constantly applied potentials of 0.9 V (vs. RHE) for 40 min, according to the following Equations (1)–(3):

\[
\text{Fe}^{3+} + 3e^- \rightarrow \text{Fe} \tag{1}
\]

\[
\text{H}_2\text{PO}_2^- + 2\text{H}^+ + e^- \rightarrow \text{P} + 2\text{H}_2\text{O} \tag{2}
\]

The reduced atoms are generally adsorbed on the electrode surface where P-atoms can diffuse and incorporate into Fe crystal lattices to develop the Fe–P phase.

\[
\text{Fe} + \text{P} \rightarrow \text{FeP} \tag{3}
\]

The developed PS-3D-FeP@NiO|Ni electrodes were rinsed with water and dried at room temperature for further electrochemical experiments. The mass loading of the PS-3D-FeP@NiO catalysts was measured to be 0.10 mg cm⁻².
For the comparison study, all other electrodes, including CoP@NiO|Ni, NiP@NiO|Ni, and CuP@NiO|Ni, were prepared using similar experimental conditions. After formation of NiO on Ni electrode, the resultant electrode was immersed in 0.1 M metal precursors (Co(NO$_3$)$_2$.6H$_2$O or Ni(NO$_3$)$_2$.6H$_2$O or CuSO$_4$) + 0.075 M sodium dihydrogen phosphate in 0.1 M nitric acid and a constant potential of 0.9 V (vs. RHE) was applied for 40 min. The developed TMP@NiO|Ni electrodes were rinsed with water and dried at room temperature for further electrochemical experiments.

The mass loading of the catalysts was computed to be ~0.10, ~0.30, ~0.40, and ~0.20 mg cm$^{-2}$ for FeP@NiO|Ni, CoP@NiO|Ni, NiP@NiO|Ni, and CuP@NiO|Ni, respectively. To fabricate the commercial IrO$_2$|Ni electrode, typically, the catalyst ink was made by combining ~10.0 mg/mL of commercial IrO$_2$ powder with 1.0 percent Nafion solution. The mixture underwent 30.0 min of ultrasonic treatment to create a uniform dispersion of IrO$_2$ catalysts. About ~10.0 µL catalyst ink dispersion was cast on nickel foam electrode (~0.81 cm$^2$), and it dried at room temperature. For the comparison, the electrochemical deposition of FeP without porous structures was developed based on the reported method [39]. Typically, the pre-cleaned nickel foam electrode that was immersed in the electrolyte solution contains a precursor mixture of 0.075 M monobasic sodium hypophosphite (NaH$_2$PO$_2$) and 0.1 M of FeCl$_3$. Five continuous cyclic voltammograms (CVs) were recorded at the cleaned NF electrode, operating the potential cycle window between ~1.63 V and ~−0.16 V (vs. RHE) at a scan rate of 5 mV s$^{-1}$. The resulting electrode was designated as the FeP|NF electrode.

2.3. Physicochemical Characterization

High-resolution transmission electron microscopic (HRTEM) study performed using a JEOL 2010F TEM. High-resolution scanning electron microscopic (HR-SEM) measurements and electron dispersive X-ray (EDX) studies were carried out with a Hitachi SU-70. X-ray diffraction (XRD) analysis was held with a Pananalytical Xpert Pro Diffractometer with a Ni filtered monochromatic Cu Kr (1.5406, 2.2 KW Max). The X-ray photoelectron spectroscopic (XPS) measurements were conducted with PHI Versaprobe III.

2.4. Electrochemical Characterization

Every electrochemical experiment was carried out using an electrochemical workstation (ORIGALYS Origoflex (OGF500) electrochem) in a three-electrode arrangement with nickel electrode (geometrical surface area: ~0.81 cm$^2$), which served as the working electrode. Pt-coil was employed as the counter electrode and silver/silver chloride (Ag/AgCl, 3.0 M KCl) was employed as the reference electrode. The present Ag/AgCl reference electrode was standardized and converted to $E_{(RHE)} = E_{(Ag/AgCl)} + 0.059 \text{pH} + E^0$, where $E^0 = 0.197 \text{V}$ at 25 $^\circ\text{C}$.

2.5. Calculation Method

The mass loading m (g cm$^{-2}$) of the catalysts and the measured current density j (A cm$^{-2}$) at different overpotential (mass activity = j/m) were used to calculate the mass activity value (A g$^{-1}$). The electrochemical active surface area (ECASA) of the developed electrodes was calculated using double-layer capacitance ($C_{dl}$) and specific capacitance ($C_S$) of 0.04 mF cm$^{-2}$, both of which were measured using cyclic voltammetry (CV) at different scan rates, starting from 10 to 125 mV s$^{-1}$. The prepared PS-3D-FeP@NiO|Ni electrode has a $C_{dl}$ of 6.31 mF cm$^{-2}$ and an ECASA of 157.7 cm$^2$, which are higher than the other electrodes [40].

$$\text{ECASA} = \frac{C_{dl}}{C_S} \quad (4)$$

The turn over frequency (TOF) was calculated using Equations (5) and (6) [41].

$$n_a = \frac{m_{\text{mass}}}{M} \quad (5)$$

$$\text{TOF} = \frac{J A}{4 F n_b} \quad (6)$$
where \( n_a \) is the number of moles of the active sites, \( m_{\text{mass}} \) is the catalyst loading, and \( M \) represents the molar mass of catalysts. \( J \) describes the current density at overpotential (\( \eta \)) of \( \sim 0.17 \) V in A cm\(^{-2}\), \( A \) is the surface area of the nickel substrate (~0.81 cm\(^2\)), \( F \) represents the Faraday constant (96,485 C mol\(^{-1}\)), and \( n_b \) is the number of electrons transferred.

3. Result and Discussion

3.1. Physicochemical Characterization of PS-3D-FeP@NiO Nanostructures

Figure 1 shows the XRD patterns of the PS-3D-FeP@NiO|Ni (a), CoP@NiO|Ni (b), NiP@NiO|Ni (c), and CuP@NiO|Ni (d) electrodes. As depicted in Figure 1a, the porous-structured 3-D FeP nanosheets dispersed on NiO electrode exhibited the peak (angle (20)) at \( \sim 32.8^\circ \), \( \sim 37.2^\circ \), and \( \sim 50.3^\circ \), which corresponded to the orthorhombic phase of FeP\(_2\) with the crystalline plane of (020), (120), and (121), respectively (JCPDS No. 89-2261) [42]. The CoP@NiO|Ni electrode (Figure 1b) showed the XRD peaks at \( \sim 31.6^\circ \) and \( \sim 36.3^\circ \), indexed to the cubic phase of CoP\(_3\) with the plane of (220), and (310), respectively (JCPDS No. 29-0496) [43]. Figure 1c displays the XRD pattern of NiP@NiO|Ni electrode presented a couple of peaks at an angle (2θ) around \( \sim 28.2^\circ \) and \( \sim 36.7^\circ \), ascribed to the hexagonal phase of Ni\(_5\)P\(_4\) with the planes of (103) and (104), respectively (JCPDS No. 18-0883) [44]. The CuP@NiO|Ni electrode demonstrated the XRD peaks at \( \sim 33.4^\circ \) and \( \sim 40.5^\circ \), ascribed to the hexagonal phase of Cu\(_2\)P with the planes (112) and (210), respectively (JCPDS No. 74-1067) [45]. In Figure 1, the other XRD peaks were marked with a star (*) and triangle (△) endorsed to the Ni and NiO electrode.

![Figure 1](image-url)

Figure 1. XRD pattern of the PS-3D-FeP@NiO|Ni (a), CoP@NiO|Ni (b), NiP@NiO|Ni (c), and CuP@NiO|Ni (d) nanostructured electrodes. The other XRD peaks were marked with a star (*) and triangle (△) endorsed to the Ni and NiO electrode.

Figure 2 displays the HR-SEM images of the nanostructured PS-3D-FeP@NiO|Ni (a), CoP@NiO|Ni (b), NiP@NiO|Ni (c), and CuP@NiO|Ni (d) electrodes. As displayed in Figure 2a and Figure S1, the PS-3D-FeP@NiO|Ni electrode showed porous-structured three-dimensional (3-D) nanosheet-like FeP dispersed on NiO modified Ni electrode. The
average dimension of 3-D FeP sphere was calculated to be ~226.0 nm with a high uniform distribution and the thickness of the FeP nanosheets was estimated to be in the range of ~7.0 nm–~9.0 nm. For our controlled study, the CoP@NiO|Ni, NiP@NiO|Ni, and CuP@NiO|Ni nanostructured electrodes were developed under similar experimental settings. The CoP@NiO|Ni electrode exhibited 2D nanoflake-structured surface morphology with an average thickness of ~8.0 nm and is shown in Figure 2b. Figure 2c shows the HR-SEM image of the nanostructured NiP@NiO|Ni electrodes, which presented the homogeneous dispersion of 2-D flake-like surface morphology. The value of the average size of the thickness of the flakes was measured to be ~12.0 nm. However, the CuP@NiO|Ni electrodes exposed the thick sheets with an average dimension of ~16.0 nm as illustrated in Figure 2d.

Figure 2. HR-SEM images of the PS-3D-FeP@NiO|Ni (a), CoP@NiO|Ni (b), NiP@NiO|Ni (c), and CuP@NiO|Ni (d) nanostructured electrodes.

Figure S2 shows the EDX spectra of the PS-3D-FeP@NiO|Ni (a), CoP@NiO|Ni (b), NiP@NiO|Ni (c), and CuP@NiO|Ni (d) nanostructured electrodes. It has been revealed that all elements including Fe, Co, Ni, Cu, and P existed in the developed electrodes in the present study. The value of atomic percentage of Fe:P, Co:P, Ni:P, and Cu:P was calculated to be 4.2:8.6, 0.4:1.5, 59.7:2.9 and 1.4:0.8 for PS-3D-FeP@NiO|Ni (a), CoP@NiO|Ni (b), NiP@NiO|Ni (c), and CuP@NiO|Ni (d) nanostructured electrodes, respectively. An elemental mapping analysis was carried out to explain the dispersion of transition metal and phosphide in all established electrodes and the following results of PS-3D-FeP@NiO|Ni (a), CoP@NiO|Ni (b), NiP@NiO|Ni (c), and CuP@NiO|Ni (d) shown in Figure 3. All the detected elements such as Fe, Co, Ni, Cu, and P were distributed uniformly throughout the electrodes.

Figure 4 shows the TEM (a and b) and HRTEM images (c) and the SAED pattern (d) of the PS-3D-FeP@NiO nanostructures. As displayed in Figure 4a,b, the PS-3D-FeP@NiO showed 3-D nanosphere-like nanosheets with the average dimension of sphere of ~34.5 nm. Figure 4c displays the HRTEM image of the PS-3D-FeP@NiO nanostructures. The interplanar distance in the selected region is calculated to be ~0.24 nm, corresponding to the (120) crystal plane of the orthorhombic FeP$_2$ [42]. The fabricated 3-D FeP@NiO nanosheets demonstrated the polycrystalline in nature, as evidenced by the SAED pattern of Figure 4d.
The 3-D FeP@NiO nanosheets presented crystalline planes of (111), (211), and (222), which reveal the polycrystallinity [42,46].

Figure 3. Elemental mapping of the PS-3D-FeP@NiO|Ni (a,b), CoP@NiO|Ni (c,d), NiP@NiO|Ni (e,f), and CuP@NiO|Ni (g,h) electrodes.

The surface elemental valence states and the elemental composition of the developed electrodes were studied by using X-ray photoelectron spectroscopy (XPS). Figure 5a displays the complete XPS survey for PS-3D-FeP@NiO|Ni electrode and confirms the presence of Fe, P, and O. As depicted in Figure 5b, a couple of XPS peaks located at 708.3 eV and 712.6 eV related with Fe 2p_{3/2} and Fe 2p_{1/2}, respectively, suggested the existence of Fe^{3+}. A broad XPS peak at 726.9 eV is ascribed to Fe^{2+} (Fe 2p_{1/2} spin-orbit) in the PS-3D-FeP@NiO|Ni electrode. Additionally, another peak at 717.9 eV is associated to the satellite peak of Fe 2p. Among them, the XPS peak obtained at 726.9 eV arises from FeP chemical
bonds, representing that P-doped Fe, which is gamely oxidized in atmosphere to develop metallic phosphate as well as the deposited Fe, exists as Fe$^{2+}$ or Fe$^{3+}$ [9,47,48]. As depicted in Figure 5c, two peaks in the P 2p region located at 132.4 eV (P 2p$_{3/2}$) and 133.6 eV (P 2p$_{1/2}$), attributed to phosphide (P) in 3-D FeP-NiO nanosheets electrode [49]. In the region of O 1s (Figure 5d), the XPS peaks at 531.1, 532.0, and 532.6 eV corresponded to the O–Fe bond, -OH bond (or O– imperfections locations), and adsorbent material oxygen at or near the electrode surface, respectively [9,31].

![Figure 4](image.png)

Figure 4. TEM image (a,b), HR-TEM (c), and SAED (d) pattern of the PS-3D-FeP@NiO nanostructures.

3.2. Electrochemical Characterization of PS-3D-FeP@NiO Nanostructures

Figure 6a depicts the cyclic voltammetric (CV) curves of the PS-3D-FeP@NiO | Ni (red curve), CoP@NiO | Ni (pink curve), NiP@NiO | Ni (black curve), and CuP@NiO | Ni (blue curve) recorded in 1.0 M KOH electrolyte at the scan rate of 20 mV s$^{-1}$ in the operating potential window of 0.74–1.64 V (vs. RHE). As shown in Figure 6a, all the as-developed electrodes presented the electrochemical redox behavior in the potential range of 1.0–1.5 V. The PS-3D-FeP@NiO | Ni electrode exhibited a strong anodic peak at ~1.27 V and cathodic peak at ~1.21 V, attributed to Fe$^{2+}$/Fe$^{3+}$ couple [50]. The CoP@NiO | Ni electrode showed two pairs of electrochemical redox peaks obtained at ~1.19 V/~1.16 V and ~1.24 V/~1.19 V, ascribed to Co$^{2+}$/Co$^{3+}$ and Co$^{3+}$/Co$^{4+}$, respectively [51]. A pair of redox peaks was observed at ~1.29 V/~1.27 V for the NiP@NiO | Ni electrode, corresponding to Ni$^{2+}$/Ni$^{3+}$ [52]. The CuP@NiO | Ni electrode showed a sharp anodic peak at more positive potential of ~1.39 V and cathodic peak at ~1.34 V, associated to Cu$^{2+}$/Cu$^{3+}$ [53].
Figure 5. (a) XPS survey spectrum of the FeP and high-resolution XPS spectra of (b) Fe 2p, (c) P 2p, and (d) O 1s spectra.

Figure 6. CV (a) and LSV (b) curves of the various electrodes including PS-3D-FeP@NiO|Ni (red curve), CoP@NiO|Ni (pink curve), NiP@NiO|Ni (black curve), and CuP@NiO|Ni (blue curve) electrodes recorded in 1.0 M KOH at the scan rate of 20 mVs⁻¹. (The arrow indicates the potential cycle started) (c) The plot of onset potentials (E_onset) and overpotential measured at 10 mA cm⁻² for PS-3D-FeP@NiO|Ni (A), CoP@NiO|Ni (B), NiP@NiO|Ni (C), CuP@NiO|Ni (D), and IrO|Ni (E) electrodes. (d) Tafel plots of the PS-3D-FeP@NiO|Ni, CoP@NiO|Ni, NiP@NiO|Ni, and CuP@NiO|Ni electrodes.
3.3. Electrochemical Catalytic OER Activity of PS-3D-FeP@NiO Nanostructures

Among all the developed electrodes, the PS-3D-FeP@NiO|Ni electrode demonstrated good redox behavior in terms of peak currents and less positive potential, favoring the electrocatalytic OER. Figure S3 shows the CV curves of the PS-3D-FeP@NiO|Ni electrode (a), CoP@NiO|Ni (b), NiP@NiO|Ni (c), and CuP@NiO|Ni (d) recorded in 1.0 M KOH at different scan rates, starting from 10 mV s\(^{-1}\) to 125.0 mV s\(^{-1}\). With increasing scan rate, the anodic and cathodic peak current densities steadily increased and maintained their shape. As depicted in Figure S4, the plot of anodic and cathodic current densities vs. the square route of scan rates showed a linear trend, indicating a mass transport process regulated by diffusion [54]. To investigate the electrocatalytic OER activity of the porous structured three-dimensional (3D) FeP nanosheets on NiO modified Ni electrode, several electrochemical techniques such as linear sweep voltammetric (LSV), chronoamperometric (CA), chronopotentiometric (CP), and electrochemical impedance spectroscopic (EIS) measurements were employed.

Figure 6b shows the LSV curves of the PS-3D-FeP@NiO|Ni (red curve), CoP@NiO|Ni (pink curve), NiP@NiO|Ni (black curve), CuP@NiO|Ni (blue curve), and commercial IrO\(_2\)|Ni (gray curve) electrodes recorded in 1.0 M KOH electrolyte at a scan rate of 20 mV s\(^{-1}\) in the operating potential range of 0.9–1.8 V (vs. RHE). As shown in Figure 6b, c, the OER onset potential was measured to be ~1.37, ~1.38, ~1.44, ~1.55, and ~1.54 V for PS-3D-FeP@NiO|Ni, CoP@NiO|Ni, NiP@NiO|Ni, CuP@NiO|Ni, and IrO\(_2\)|Ni electrodes, respectively. The value of overpotential (\(\eta\)) was measured at the current density of ~10.0 mA cm\(^{-2}\) to be ~0.17, ~0.18, ~0.29, ~0.38, and ~0.24 V for PS-3D-FeP@NiO|Ni, CoP@NiO|Ni, NiP@NiO|Ni, CuP@NiO|Ni, and IrO\(_2\)|Ni electrodes, respectively. Besides the OER onset potential and overpotential, the anodic current density was calculated at the potential of ~1.80 V to be ~580, ~365, ~145, ~185, ~516, and 310 mA cm\(^{-2}\) for PS-3D-FeP@NiO|Ni, CoP@NiO|Ni, NiP@NiO|Ni, CuP@NiO|Ni, IrO\(_2\)|Ni, and FeP\(_2\)|NF electrodes, respectively. The porous structured 3D FeP nanosheets on NiO modified Ni electrode demonstrated a highest current density of ~580 mA cm\(^{-2}\) at ~1.80 V in comparison to other electrodes employed in the current investigation (Figure 6 and Figure S5). The PS-3D-FeP@NiO|Ni electrode exhibited higher OER catalytic current densities over ~1.6, ~4.0, ~3.1, and ~1.1-times greater than that of the CoP@NiO|Ni, NiP@NiO|Ni, CuP@NiO|Ni, and IrO\(_2\)|Ni electrodes, respectively.

Figure 6d presents the Tafel plots of the PS-3D-FeP@NiO|Ni, CoP@NiO|Ni, NiP@NiO|Ni, CuP@NiO|Ni, and IrO\(_2\)|Ni electrodes, which is fitted in the strongly polarized area of the LSV curves. It is understood that a smaller Tafel slope is beneficial for the practical application of catalysts in electrode materials because it leads to faster catalytic reaction kinetics and greater charge transfer abilities. The Tafel slope values for PS-3D-FeP@NiO|Ni, CoP@NiO|Ni, NiP@NiO|Ni, CuP@NiO|Ni, and IrO\(_2\)|Ni electrodes were determined to be ~40.0, ~59.0, ~90.0, ~60.0 and ~63.0 mV dec\(^{-1}\), respectively. Among the developed electrodes in the present study, the PS-3D-FeP@NiO|Ni exhibited the smallest Tafel slope when compared to other electrodes, indicating the faster catalytic oxygen evolution kinetics and greater charge transfer abilities than other materials employed in this work.

Figure 7 depicts the Nyquist plots of the PS-3D-FeP@NiO|Ni, CoP@NiO|Ni, NiP@NiO|Ni, CuP@NiO|Ni, and IrO\(_2\)|Ni electrodes at the applied potential of ~1.49 V. As shown in Figure 7, the PS-3D-FeP@NiO|Ni (A) exhibited the lowest polarization resistance (\(R_p\)) (~3.3 \(\Omega\)) in comparison to other electrodes CoP@NiO|Ni (B) (~3.9 \(\Omega\)), NiP@NiO|Ni (C) (~12.3 \(\Omega\)), and CuP@NiO|Ni (D) (~6.5 \(\Omega\)) electrodes developed in this study. In addition, the PS-3D-FeP@NiO|Ni demonstrated a high double layer capacitance (\(C_{dl}\)) of ~40. 5 mF cm\(^{-2}\), indicating accelerated charge transfer and mass diffusion processes at the electrode/electrolyte (Table S1).
Figure 7. Nyquist plots of the nanostructured PS-3D-FeP@NiO@Ni (A) (red curve), CoP@NiO@Ni (B) (pink curve), NiP@NiO@Ni (C) (black curve), and CuP@NiO@Ni (D) (blue curve) electrodes recorded at the applied potential of ~1.49 V in 1.0 M KOH.

Figure 8 displays the multi-step chronoamperometric (a) and chronopotentiometric (b) techniques to examine the electrocatalytic OER activity of the designed PS-3D-FeP@NiO@Ni nanostructured electrode at different applied potentials ($E_{app}$) and applied currents ($i_{app}$) under alkaline electrolyte. The PS-3D-FeP@NiO@Ni electrode delivered high steady-state current density of ~55.1, ~123.2, ~195.3 and ~270.5 mA cm$^{-2}$ at applied potentials of 1.58, 1.63, 1.68, and 1.73 V, respectively, as shown in Figure 8b. Furthermore, the PS-3D-FeP@NiO@Ni electrode exhibited low electrode potentials of ~1.58, ~1.62, ~1.66 and ~1.67 V at the applied current densities of ~50.0, ~100.0, ~150.0, and ~200.0 mAcms$^{-2}$, respectively (Figure 8c,d). The electrochemical active surface area (ECASA) of the PS-3D-FeP@NiO@Ni electrode was calculated based on their double-layer capacitance ($C_{dl}$) and is shown in Figure S6. The value of $C_{dl}$ was established to be 6.31 mF cm$^{-2}$, revealed that the PS-3D-FeP@NiO@Ni electrode showed high double layer capacitance and a high ECASA due to the porous-structured 3D nanosheets-like surface morphology.

Based on these practical attentions, the OER CV curves were captured at the PS-3D-FeP@NiO@Ni electrode under 30% KOH electrolyte and are displayed in Figure S8. The CV and LSV curves of the PS-3D-FeP@NiO@Ni electrode delivered the overpotential of 0.20 V at a current density of 10 mA cm$^{-2}$ (Figure S7). As summarized in Table 1, the as-developed PS-3D-FeP@NiO@Ni electrode delivered a lowest onset OER potential, overpotential, and high TOF values in comparison to other electrodes reported in the literature. The excellent OER electrocatalytic characteristics correspond to porous-structured 3D nanosheets of FeP@NiO on Ni electrode, which offer rich active sites, large volume of ECASA, and improved conductivity. In addition, the synergistic effect among FeP and NiO heterostructures would facilitate the charge transfer kinetics and ion diffusion.
The long-standing stability of the designed nanostructured PS-3D-FeP@NiO|Ni electrode was studied using chronopotentiometric measurements in 1.0 M KOH for 24 h by operating a constant current density of ~10.0 mA cm$^{-2}$ and is presented in Figure S9. After a 24-h continuous OER measurement, the PS-3D-FeP@NiO|Ni nanostructured electrode retained OER activity with an electrode potential of ~1.56 V, revealing good stability. The inset in Figure S8 displays the LSV curves of the three-brand new developed PS-3D-FeP@NiO|Ni electrodes recorded in 1.0 M KOH. As depicted in Figure S8 (inset), the PS-3D-FeP@NiO|Ni electrodes exhibited a stable polarization curve and delivered a similar overpotential of 0.172 V (red curve), 0.176 V (black curve), and 0.177 V (blue curve) at the current density of ~10.0 mA cm$^{-2}$, suggesting good reproducibility.
As displayed in Figures 9 and S9, the surface morphology of the 3D-FeP@NiO|Ni electrode had not altered after a long-term durability test conducted under an alkaline electrolyte. The EDS results suggested that the chemical composition, distribution of Fe, P, and O, and crystalline structures were not altered significantly. The ECASA of the PS-3D-FeP@NiO|Ni electrode was calculated after a long-term durability test and is shown in Figure S10. The value of $C_{dl}$ and ECASA was established to be 2.67 mF cm$^{-2}$ and 66.7 cm$^2$, respectively, revealing that the ECASA for PS-3D-FeP@NiO|Ni electrode was reduced after a long-term stability test due to the adsorption of intermediates on the catalyst surface.

![Figure 9. TEM images of the low magnification (a) and high magnification (b), HRTEM image (c), and SAED pattern (d) for the PS-3D-FeP@NiO|Ni electrode measured after a long-term stability test.](image)

Moreover, to demonstrate the practicability, full cell alkaline electrolysis was prepared using the PS-3D-FeP@NiO|Ni || Pt/C couple in 1.0 M KOH. For the purpose of comparison, the state-of-the-art IrO$_2$ || Pt/C couple was also prepared. As depicted in Figure 10, the present PS-3D-FeP@NiO|Ni || Pt/C (red curve) couple exhibited a low cell voltage of ~1.66 V at a current density of 10 mA cm$^{-2}$ and delivered a high current density of ~294.0 mA cm$^{-2}$ at the potential of ~2.0 V, showing high performance for practical feasibility. On the other hand, the state-of-the-art IrO$_2$ || Pt/C couple (gray curve) delivered a cell potential of ~1.70 V at the current density of 10 mA cm$^{-2}$ and exhibited the current density of ~219.0 mA cm$^{-2}$ at the potential of ~2.0 V.
Figure 10. LSV curves of the PS-3D-FeP@NiO|Ni || Pt/C (red curve) and state-of-the-art IrO₂ | Ni || Pt/C (grey curve) couple for overall water splitting recorded in 1.0 M KOH at a scan rate of 20 mV s⁻¹.

4. Conclusions

In summary, porous structured three-dimensional (3-D) FeP nanosheets on NiO modified Ni electrode is developed using of a simple method and two-step electrodeposition strategy. For comparison, a series of other nanostructured transition metal (cobalt, nickel, and copper)-derived phosphides on nickel oxide (NiO) modified Ni electrode is developed under similar experimental settings. The fabricated PS-3D-FeP@NiO|Ni electrode exhibits the best electrocatalytic activity towards OER under alkaline electrolyte with low onset potential (~1.37 V (vs. RHE)), small overpotential (η) (~0.17 V to produce the current densities of 10 mA cm⁻²), small Tafel slope (~40.0 mV dec⁻¹), high turn-over frequency (TOF) (0.435 s⁻¹), and long-term stability among the developed CoP@NiO|Ni, NiP@NiO|Ni, CuP@NiO|Ni, and commercial IrO₂|Ni electrodes. The outclassing OER activity of PS-3D-FeP@NiO|Ni is allied to its porous-structured 3-D sheet-like morphology, a large quantity of electrochemical active surface area, high electrical conductance characteristics and self-activated/supported active sites, facilitating the catalytic properties towards OER. The surface morphology, crystalline structure, chemical composition, and distribution of Fe, P and O elements have not been altered significantly after a long-term OER test. This fabrication route may be expanded to produce a variety of bi-metallic and tri-metallic phosphides for electrochemical energy conversion and storage systems.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/en16031124/s1, Table S1. EIS data derived from Nyquist plots of Figure 7; Figure S1. HR-SEM images of FeP nanostructures with high (a) and low (b) magnification images; Figure S2. EDX spectra of the PS-3D-FeP@NiO|Ni (a), CoP@NiO|Ni (b), NiP@NiO|Ni (c), and CuP@NiO|Ni (d) electrodes; Figure S3. CV curves of the PS-3D-FeP@NiO|Ni (a), CoP@NiO|Ni (b), NiP@NiO|Ni (c), and CuP@NiO|Ni (d) electrodes recorded in 1.0 M KOH with the different scan rates, starting from 10 to 125 mV s⁻¹; Figure S4. The plot of anodic and cathodic peak current densities against the square root of the scan rates for PS-3D-FeP@NiO|Ni (a), CoP@NiO|Ni (b), NiP@NiO|Ni (c), and CuP@NiO|Ni (d); Figure S5. CV (a) and LSV (b) curves of the PS-3D-FeP@NiO|Ni (red curve) and FeP|NF (black curve) electrodes recorded in 1.0 M KOH electrolyte; Figure S6. (a) CVs of the PS-3D-FeP@NiO|Ni electrode recorded in 1.0 M KOH at different scan rates from 10 to 125 mV s⁻¹. (b) Plot of current density measured from non-faradaic region of the voltammograms against the function.
of the scan rates; Figure S7. CV curve (a) and LSV curves (b) of the PS-3D-FeP@NiO|Ni electrode recorded in 30% KOH. Figure S8. Chronopotentiometric curve of the PS-3D-FeP@NiO|Ni electrode recorded in 1.0 M KOH under applied current density of ~10.0 mA cm⁻². Inset: LSV curves of the PS-3D-FeP@NiO|Ni electrodes. Electrolyte: 1.0 M KOH; Scan rate of 20 mV s⁻¹; Figure S9. HR-SEM image (a), EDX spectra (b) and elemental mapping of Fe, P and O (c) for the PS-3D-FeP@NiO|Ni electrode measured after had a long-term stability test; Figure S10. (a) CVs of the PS-3D-FeP@NiO|Ni electrode recorded in 1.0 M KOH at different scan rates from 10 to 125 mV s⁻¹ measured after had a long-term stability test. (b) Plot of current density measured from non-faradaic region of the CVs against the function of the scan rates.

Author Contributions: G.M. designed the study; S.M. and A.S. performed the experimental work; S.M. analyzed the results and drafted the manuscript; G.M. discussed and corrected the manuscript. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by a CPRI, Bangalore (Ref. No.: CPRI/R&D/TC/GDEC/2022).

Data Availability Statement: Not applicable.

Acknowledgments: We acknowledge by the SRM Institute of Science and Technology (SRM IST) for providing all the research facilities, including SRM-SCIF for HRTEM, HRSEM, and XRD measurements. This work was commercially supported by the Central Power Research Institute (CPRI), Bangalore (Ref.: CPRI/R&D/TC/GDEC/2022).

Conflicts of Interest: The authors declare no conflict of interest.

References


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