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Electrodeposited Nanostructured CoFe$_2$O$_4$ for Overall Water Splitting and Supercapacitor Applications

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Abstract: To contribute to solving global energy problems, a multifunctional CoFe$_2$O$_4$ spinel was synthesized and used as a catalyst for overall water splitting and as an electrode material for supercapacitors. The ultra-fast one-step electrodeposition of CoFe$_2$O$_4$ over conducting substrates provides an economic pathway to high-performance energy devices. Electrodeposited CoFe$_2$O$_4$ on Ni-foam showed a low overpotential of 270 mV and a Tafel slope of 31 mV/dec. The results indicated a higher conductivity for electrodeposited compared with dip-coated CoFe$_2$O$_4$ with enhanced device performance. Moreover, bending and chronopotentiometry studies suggest excellent durability of the catalytic electrode for long-term use. The energy storage behavior of CoFe$_2$O$_4$ showed high specific capacitance of 768 F/g at a current density of 0.5 A/g and maintained about 80% retention after 10,000 cycles. These results demonstrate the competitiveness and multifunctional applicability of the CoFe$_2$O$_4$ spinel to be used for energy generation and storage devices.

Keywords: CoFe$_2$O$_4$; OER; HER; supercapacitor; overall water splitting

1. Introduction

According to the report presented by the International Renewable Energy Agency (IRENA), the Renewable Energy Policy Network for the 21st Century (REN21), and the International Energy Agency, transport is the second largest energy end-use sector, accounting for 29% of the total final energy consumption in the year 2015 [1]. About 96% of this energy comes from petroleum products, making it heavily reliant on fossil fuels. Several companies such as Tesla, Toyota, Nissan, Mercedes-Benz, Hyundai, Honda, and others have targeted their automotive market in the way that global dependence on petroleum...
resources is reduced [2,3]. Thus, major research focuses on multifunctional materials for green energy applications to be used for electric motor and fuel cell vehicles.

Spinel has recently attracted considerable research attention for energy applications [4–6]. They represent a group of composite metals with such multifunctional capabilities, having a formula of AB₂O₄ (A and B are metal ions) [7]. Mixed phase composition of transition metals into spinel structure provides advantageous electrical and catalytic properties required characteristics for energy conversion and storage [4–6]. Previously, electroactive materials such as structured carbons [8–14], transition metal oxides, and sulfides [15–18] have been studied for applications in batteries, supercapacitors, and fuel cells, as well as for water splitting. However, the lower activity of carbon-based materials, the inferior electronic conductivity of transition metal oxides, and the poor stability of transition metal sulfides limit their applicability for future energy devices [14,19–21]. Transition metal-based systems including oxides, hydroxides, or sulfides of cobalt and iron have been studied in the past few years for energy conversion or storage applications [22–27]. However, these materials show limited electrochemical performance. Various studies suggest that spinels of cobalt and iron provide better electronic conductivity, a higher population of active sites, and thus better electrochemical performance. For example, Kumbhar et al. synthesized spinel CoFe₂O₄ nano-flakes on a stainless steel substrate by a simple chemical route using an alkaline bath containing Co²⁺ and Fe²⁺ ions for supercapacitor application [28]. An impedance test of spinel electrodes showed the low equivalent series resistance of about 1.1 Ω. Yu et al. reported a novel hierarchical Cu on a CoFe layered double hydroxide (LDH) core-shell nanostructured catalyst for oxygen and hydrogen evolution reaction [29]. The unique structure of LDH provides more active sites, leading to better catalytic performance. Another report suggests the use of iron–cobalt oxide nanosheets (FeₓCoᵧ-ONSs) as a stable water oxidation catalyst [30]. Excellent oxygen evolution reaction (OER) activity was observed as a result of mass diffusion/transport of OH⁻ ions facilitated by ultrathin nanosheets, improved electronic conductivity, and adsorption of H₂O onto close Co³⁺ sites.

Several methods such as solvothermal, hydrothermal, chemical co-precipitation, and solution reduction reaction are reported for the synthesis of iron–cobalt oxide [30–35]. Most of the synthesized iron–cobalt oxide samples were powders, which are coated onto conductive substrates by dip-coating. The use of electrically insulating binders reduces the conductivity and thus affects the electronic activity of the material. Furthermore, the stability and flexibility of the electrodes are also compromised. However, direct electrodeposition of materials on conductive substrates could overcome this problem. For example, Lu et al. fabricated a hierarchically structured three-dimensional nickel-iron composite on Ni-foam for efficient oxygen evolution catalyst electrode using a one-step electrodeposition [36]. Higher conductivity and active surface area of the material over the electrode resulted in better electrochemical performance.

In this work, CoFe₂O₄ was deposited on Ni-foam and carbonized cotton cloth using a facile electrodeposition method. The synthesized CoFe₂O₄ on Ni-foam exhibited high electrocatalytic activity for OER and hydrogen evolution reaction (HER) with small overpotential. In addition, the CoFe₂O₄ electrode showed high specific capacitance of 768 F/g at the current density of 0.5 A/g, maintaining stable performance with 80% retention up to 10,000 charge–discharge cycles. Our results suggest that electrodeposited CoFe₂O₄ on Ni-foam could be used as a multifunctional material for both water splitting and supercapacitor applications.

2. Results and Discussion

X-ray diffraction (XRD) was used to study phase purity and crystallinity of the synthesized samples. Figure S1 shows the XRD patterns of CoFe₂O₄, CoFe₂O₄ ED@NF, and CoFe₂O₄ ED@carbonized cotton cloth (CCC). The XRD pattern of CoFe₂O₄ shows characteristic peaks of (111), (220), (311), (400), (422), (511), (440), and (533) planes, corresponding to the cubic structure of FeCo₂O₄. No peaks other than those stemming from CoFe₂O₄ were observed, confirming phase purity of the synthesized CoFe₂O₄. The XRD patterns of CoFe₂O₄ ED@NF and CoFe₂O₄ ED@CCC do not show any
peaks attributable to CoFe$_2$O$_4$, indicating either the amorphous nature of the electrodeposited CoFe$_2$O$_4$ layer or the lack of sufficient diffracted X-ray signal from the coating on the porous Ni-foam structure.

An X-ray photoelectron spectroscopy (XPS) wide scan of the CoFe$_2$O$_4$ surface is presented in Figure S2. The Co 2p and O 1s peaks are given in Figure 1. Considering the Co 2p peak shape, this is very consistent with spectra of Co$_3$O$_4$ standards given by Gu et al. [37] and Yang et al. [38], showing a 2p$_{3/2}$ peak binding energy of 779.9 eV and a broad plateau-like satellite structure to higher binding energies between the 2p$_{3/2}$ and 2p$_{1/2}$ Peaks. Thus, this peak shape and satellite structure is representative of mixed Co$^{2+}$/Co$^{3+}$ chemical states. Compared with the Co 2p spectrum for CoFe$_2$O$_4$ given by Gu et al. [37] and Sagu et al. [39], the peak shape of the electrodeposited CoFe$_2$O$_4$ shows a peak shape that is more consistent with that of Co$_3$O$_4$, and hence a 1:1 stoichiometric Co$^{2+}$/Co$^{3+}$ fraction rather than the Co$^{2+}$ rich compound observed in these other studies. However, it should be noted that quantification of the XPS spectra shows an enrichment of Co at the surface, indicating that the XPS spectra and outermost surface composition are not fully representative of the bulk material. The O 1s spectrum (Figure 1b) shows a peak at 530.1 eV corresponding to the metal oxide, with peaks at 531.6 and 532.7 eV corresponding to hydroxyl and adsorbed water species, respectively.

![Figure 1: X-ray photoelectron spectroscopy (XPS) core level spectra of (a) Co 2p and (b) O 1s.](image)

Figure 2a–c present scanning electron microscopy (SEM) images of electrodeposited CoFe$_2$O$_4$ over Ni-foam at different magnifications. The coating over the Ni-foam is relatively uniform and dense, as observed from the images. The cracks in the coating are most likely the result of dehydration, associated with removal of the electrode from solution. The energy dispersive X-ray spectroscopy (EDS) O elemental image in Figure 3 confirms the general uniform distribution and composition of CoFe$_2$O$_4$ layer over the Ni-foam substrate. However, the Fe and Co images in Figure 3 show that there are differences in the Fe/Co ratio between the ‘smoother’ surface regions and underlying ‘mottled’ areas of the coating. Considering the XPS results, it seems most likely that the smooth outer layer is CoFe$_2$O$_4$ and this predominantly covers the Ni-foam. However, in some areas, this layer has become detached (possibly because of stresses associated with dehydration or transfer to the analytical laboratory), exposing a more Co-rich underlying layer. SEM images for CoFe$_2$O$_4$ electrodeposited on CCC are given in Figure S3a–c, evidencing evenly coated fibers.

The OER activity of the CoFe$_2$O$_4$ samples was studied by linear sweep voltammetry (LSV). The polarization curves for CoFe$_2$O$_4$ ED@NF, CoFe$_2$O$_4$@NF, and CoFe$_2$O$_4$ ED@CCC in 1M NaOH are shown in Figure 4a. The CoFe$_2$O$_4$ ED@NF electrode required a low overpotential of 270 mV to achieve a current density of 10 mA/cm$^2$. This value is significantly lower than for CoFe$_2$O$_4$@NF (308 mV) and CoFe$_2$O$_4$ ED@CCC (410 mV) electrodes. The observed difference could be the result of the high conductive pathway between the CoFe$_2$O$_4$ catalyst and the Ni-foam, compared with the electrode synthesized by dip-coating. The Nyquist plot in Figure 4c at 0.5 V (versus SCE) shows lower charge transfer resistance for the CoFe$_2$O$_4$ ED@NF electrode, which could be responsible for better catalytic
performance over other synthesized electrodes. The reduced impedance over increasing potential can be observed from the Nyquist plot for the CoFe$_2$O$_4$ ED@NF electrode given in Figure S4. The kinetics of the OER reaction were analyzed using Tafel slopes (Figure 4b). The Tafel slope for CoFe$_2$O$_4$ ED@NF, CoFe$_2$O$_4$@NF, and CoFe$_2$O$_4$ ED@CCC was calculated to be 31, 47, and 119 mV/dec, respectively. The low Tafel slope value for the CoFe$_2$O$_4$ ED@NF electrode indicates faster OER kinetics and can be correlated to the high electrocatalytic surface area of the electrodeposited Ni-foam electrode [15]. The electrochemical effective surface area was calculated using cyclic voltammetry (CV) curves in the non-faradic region (Figure S5) and the plotting relation of current density with respective scan rate is given in Figure 4d. A linear relationship was observed, showing a higher slope for CoFe$_2$O$_4$ ED@NF (65 mC/cm$^2$) than CoFe$_2$O$_4$@NF (40 mC/cm$^2$) and CoFe$_2$O$_4$ ED@CCC (3 mC/cm$^2$), thus indicating a larger effective electrochemical surface area. The higher surface area of CoFe$_2$O$_4$ ED@NF is consistent with the excellent OER performance. The CoFe$_2$O$_4$ ED@NF electrode of this study required a lower overpotential for achieving a current density of 10 mA/cm$^2$ compared with other FeCo-based reports. For example, Yan et al. synthesized a CoFe$_2$O$_4$ hybrid strongly coupled with carbon nanotubes and observed a higher overpotential (>0.6 V) to achieve 5 mA/cm$^2$ in 0.1 M KOH [31]. Another hybrid of CoFe$_2$O$_4$ nanoparticles supported on nitrogen/sulfur dual-doped three-dimensional (3D) reduced graphene oxide networks (CFO/NS-rGO) showed an overpotential of about 0.55 V to achieve the current density of 10 mA/cm$^2$ [32]. The iron–cobalt oxide nanosheets (FeCo-ONS) prepared by Zhuang et al. required an overpotential of 308 mV to reach 10 mA/cm$^2$ with a Tafel slope of 36.8 mV/dec [30].

Table S1 shows a detailed comparison of catalytic electrodes synthesized within this work with previously reported CoFe$_2$O$_4$ samples. It can be observed that the CoFe$_2$O$_4$ ED@NF electrode requires a low overpotential and shows higher kinetics of reaction compared with all the other reported values.

**Figure 2.** Scanning electron microscopy (SEM) images of electrodeposited CoFe$_2$O$_4$ on Ni-foam.

**Figure 3.** EDX elemental maps of electrodeposited CoFe$_2$O$_4$ on Ni-foam revealing the distribution of Co, Fe, and O.
The effect of bending on the OER properties of the CoFe$_2$O$_4$ ED@NF electrode was studied to investigate its potential to be used as a flexible electrode. The polarization curves in Figure 5a show almost identical behavior for curves before and after bending the electrode by a 60° angle. Moreover, the durability of the electrode was assessed for 17 h using chronoamperometry (Figure 5b). The chronical current measurement showed almost constant values without any detriment over the catalytic performance of the electrodes, suggesting the durable performance of the electrode for long-term use.

Figure 4. (a) Polarization curves, (b) Tafel slopes, (c) Nyquist plot at 0.5 V (vs. SCE), and (d) current density vs. scan rate plots for CoFe$_2$O$_4$ electrodes. RHE—reversible hydrogen electrode; CCC—carbonized cotton cloth.

Figure 5. (a) Bending test and (b) chronoamperometry data for CoFe$_2$O$_4$ ED@NF in oxygen evolution reaction (OER) range.
As several reports suggest the use of spinels for multifunctional catalytic application [7, 31, 40], herein we evaluated the performance of the CoFe$_2$O$_4$ ED@NF electrode for HER catalysis. Figure 6a shows the LSV polarization curves. A small overpotential of $-270$ mV was required to achieve the current density of $-10$ mA/cm$^2$. Moreover, the reaction kinetics using the Tafel slope yielded a low value of $94$ mV/dec (Figure 6b). The value observed for the CoFe$_2$O$_4$ electrode as HER catalyst was lower compared with other similar catalytic systems. For example, a hydrothermally synthesized CoFe$_2$O$_4$ NPs-on-CFP electrode by Kargar and co-workers required an overpotential of $-356$ mV to achieve a current of $-10$ mA/cm$^2$ [41]. The comparison table of other reports based on Fe, Co, and other non-precious transition metals in alkaline media can be observed from Table S2. Moreover, the chronoamperometry test indicated a stable HER performance of the catalyst electrode for 17 h, suggesting long-term durability of the electrode (Figure 6c). This indicates that the CoFe$_2$O$_4$ ED@NF electrode could be used as a bifunctional water-splitting catalyst.

An electrolyzer cell was fabricated using a two-electrode system to study water-splitting of catalytic electrodes. In this study, the CoFe$_2$O$_4$ ED@NF electrode was used as an anode and a standard platinum carbon (Pt–C) electrode was used as a cathode. Figure 6a shows polarization curves using the LSV test for different electrolyzer cells. The CoFe$_2$O$_4$ //Pt-C electrolyzer system required a low potential of $1.56$ V to obtain a current density of $10$ mA/cm$^2$ compared with benchmark electrolyzer cells such as IrO$_2$/Pt–C (1.57 V), IrO$_2$/IrO$_2$ (1.77 V), and Pt–C//Pt–C (1.64 V), which all required higher potentials. Moreover, the chronoamperometry test yielded stable performance of the CoFe$_2$O$_4$//Pt-C electrolyzer system for more than 17 h, as evidenced by Figure 6b.

The energy storage capacity of the CoFe$_2$O$_4$ ED@NF electrode was measured using CV. The specific capacitance values can be predicted based on the area under the CV curves. Figure 7a depicts the specific capacitance values as a function of varying scan rates. Higher specific capacitance values were observed with decreasing scan rates. A similar behavior was observed in other reports of energy storage systems [28, 42–44]. The CV curves of CoFe$_2$O$_4$ ED@NF in 3M KOH electrolyte at various scan rates are given in Figure S7a. Pairs of redox peaks in the CV curves indicate the pseudocapacitive behavior of the material. This resulted in a high specific capacitance of 2246 F/g at a scan rate of 1 mV/s. The charge storage behavior was further analyzed using the galvanostatic charge–discharge test. Figure 7b shows the relationship of specific capacitance at different current densities. At lower charging current, high capacitance values were obtained. A similar relation of current density with discharge time can be observed from Figure S7b. This could be the result of sufficient time provided for redox reactions at low current densities. Redox reactions promoted at low current densities lead to better charge storage compared with other non-faradic systems [43–46]. At a current density of 0.5 A/g,
a high specific capacitance of 768 F/g was observed. This result is comparable to other reported values for electrodes within an Co–Fe based system, as summarized in Table S3. Moreover, the stability test of the electrode showed high capacitance retention of about 80% after 10,000 cycles (Figure S8), which is better compared with other reports based on Co–Fe systems. For example, flower-like CoFe2O4/FeOOH nanocomposites maintain 91.3% retention after 1000 cycles [47]. For reduced graphene oxide–CoFe2O4 composites, the capacitance retention is about 78.1% after 1000 cycles [35]. This suggests that the synthesized CoFe2O4 ED@NF electrodes showed higher charge storage capacities and stable performance to be used as energy storage electrode materials.

![Figure 7. Variation of specific capacitance as a function of (a) scan rate and (b) current density for FeCo2O4 ED@Ni-foam.](image)

3. Materials and Methods

3.1. Materials

All chemicals were of analytical grade purity and were used without any further purification. Cobalt (II) nitrate and iron (III) nitrate (99.9%) were purchased from Sigma Aldrich, USA. All other chemicals were purchased from Fisher Scientific, USA.

3.2. Preparation of Electrodeposited CoFe2O4 Electrodes

Nanostructured CoFe2O4 was electrodeposited on Ni-foam and carbonized cotton cloth (CCC) using a standard three-electrode system. Before electrodeposition, Ni-foam was thoroughly cleaned [15]. In the three-electrode system, Ni-foam as a working electrode, a platinum plate as a counter electrode, and an Ag/AgCl electrode as a reference electrode were used. The electrolyte consists of an aqueous solution of 0.582 g of cobalt nitrate and 1.616 g of iron nitrate in 20 ml deionized water. The electrodeposition was carried out at −1.0 V (vs. Ag/AgCl) for a period of 5 min to obtain a thin brown film covering the Ni-foam [48]. The average weight of the deposited material was 1.2 mg/cm².

Electrodeposition of CoFe2O4 on the CCC was carried out using the above setup, where CCC was used instead of Ni-foam as a substrate. The CCC was prepared by calcination of carbon cloth in a tube furnace at 800 °C for two hours under N₂ atmosphere (at 5 °C/min) [49]. Electrodeposition of CoFe2O4 on CCC was carried out under similar conditions, but for 50 min to achieve 1.2 mg/cm² of the deposited material.

3.3. Preparation of Dip-Coated CoFe2O4 Electrode

To compare the effect of the direct growth of CoFe2O4 on a conducting surface, we have dip-coated CoFe2O4 powders on the Ni-foam after synthesizing CoFe2O4. For this reason, CoFe2O4 was synthesized by a simple hydrothermal method, where 0.582 g of cobalt nitrate, 1.616 g of iron nitrate, and 7.2 g of urea were dissolved in a mixture of 30 ml of isopropyl alcohol and 6 ml of water. The mixture was stirred for 30 min and transferred into a 45 mL Teflon-lined stainless-steel
autoclave. The reaction was carried out at 120 °C for 12 h. The resultant precipitates were washed several times using water and ethanol. The separation was carried out using centrifugation at 10,000 rpm, followed by drying under vacuum at 80 °C for 6 h and calcination at 350 °C in air for 2 h (5 °C/min). The CoFe₂O₄ electrode was prepared by dipping the Ni-foam in a slurry of CoFe₂O₄ powder (80 wt.%), acetylene black (10 wt.%), and polyvinylidene difluoride (10 wt.%) in N-methyl pyrrolidinone. The material loading on the Ni-foam was about 1.2 mg/cm². Sample electrodes fabricated by deposition of CoFe₂O₄ over Ni-foam using electrodeposition and dip-coating are termed in the following as CoFe₂O₄ ED@NF and CoFe₂O₄@NF, respectively, while the sample electrodeposited over carbonized carbon cloth is referred to as CoFe₂O₄ ED@CCC.

3.4. Characterization

The synthesized samples were characterized using various methods. X-ray diffraction (XRD) was used to study the crystallinity and phase purity of the samples. X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectroscopy (EDS) was used to investigate structural, chemical, and morphological properties. XRD patterns were recorded using a Shimadzu X-ray diffractometer (Lenexa, Kansas, USA). CuKα radiation (λ = 1.5406 Å) in the 2θ-θ mode was used to study the crystallinity and phase purity of the synthesized samples. Microstructural properties of the samples were investigated using a Quanta 200 SEM (FEI, Hillsboro, Oregon, USA). The elemental compositions and elemental mapping of the synthesized samples were recorded for the synthesized samples using EDS. The chemical composition of the synthesized samples was determined using XPS analysis using a ThermoFisher Scientific Instruments (East Grinstead, UK). A monochromated Al Kα radiation source (hv = 1486.6 eV) and an X-ray spot of ~400 µm in radius were used for data recording. The elemental survey spectra were recorded using a pass energy of 200 eV. A passing energy of 50 eV was used for recording high-resolution core level spectra for all the elements. The Advantage software was used for the peak fittings.

Electrochemical performance was studied using a standard three-electrode system and a Versastat4-500 electrochemical workstation (Princeton Applied Research, TN, USA). CoFe₂O₄ electrodes were used as working electrodes. Cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS) measurements were performed to examine the energy storage performance of electrodes in 3M KOH electrolyte. The electrocatalytic behavior of the CoFe₂O₄ electrodes for OER and HER was measured in 1M NaOH electrolyte. Electrocatalytic testing includes linear sweep voltammetry (LSV), cyclic voltammetry (CV), chronoamperometry, and electrochemical impedance spectroscopy (EIS). LSV was performed at a scan rate of 1 mV/s in both the OER and HER region. The potential was converted to a reversible hydrogen electrode (RHE) using the Nernst equation. All the EIS measurements were recorded in a frequency range of 0.05 Hz to 10 kHz with an applied 10 mV of AC amplitude.

4. Conclusions

In summary, we synthesized an efficient catalyst and energy storage material using a facile, ultra-fast, and one-step electrodeposition method to grow CoFe₂O₄ over Ni-foam and carbon cloth. A uniform distribution of CoFe₂O₄ electrochemically deposited over the surface of the substrate was observed through SEM and EDX. A low overpotential of 270 mV was calculated for OER when CoFe₂O₄ was grown over Ni-foam using electrodeposition. The obtained low Tafel slope of 31 mV/dec compared with a dip-coated sample represents excellent reaction kinetics. This could be attributed to a high conductive pathway stemming from the CoFe₂O₄ deposited over Ni-foam. Flexibility and chronoamperometry evidenced the stable catalytic performance of the electrodes. The energy storage capacity of the material using galvanostatic charge-discharge test show high specific capacitance of 768 F/g at a current density of 0.5 A/g. Stability of electrodes after 10,000 cycles showed capacitance retention of 80%. The obtained results reveal the promising potential of efficient, multi-functional, and cost-effective CoFe₂O₄ catalysts for energy generation and storage systems.
Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/9/2/176/s1, Figure S1. XRD patterns of (a) CoFeO$_4$, (b) CoFe$_2$O$_4$ ED@CCC and CoFe$_2$O$_4$ ED@NF. Figure S2. XPS wide scan of the CoFe$_2$O$_4$. Figure S3. SEM images of electrodeposited CoFe$_2$O$_4$ on carbonized carbon cloth. Figure S4. Nyquist plots for the CoFe$_2$O$_4$ ED@NF sample at various potentials (vs. SCE). Figure S5. CV curves in non-faradic region for (a) CoFe$_2$O$_4$ ED@NF, (b) CoFe$_2$O$_4$@NF, and (c) CoFe$_2$O$_4$ ED@CCC. Figure S6. (a): Polarization curves, (b) Tafel slopes, and (c) chronoamperometry data for CoFe$_2$O$_4$ ED@NF in HER range. Figure S7. (a) CV curves and (b) GCD curves of CoFe$_2$O$_4$ ED@NF obtained at various scan rates and current densities in 3M KOH electrolyte. Figure S8. Cyclic stability plot for CoFe$_2$O$_4$ ED@NF sample using 10,000 galvanostatic charge-discharge measurements. Table S1. Comparison of OER performance of some recently reported FeCo-based electrocatalysts. Table S2. Comparison of HER performance of some recently reported electrocatalysts in alkaline media. Table S3. Comparison of specific capacitances of some reported FeCo-based samples.

Author Contributions: R.K.G. conceived the project, designed the experiments, interpreted the data, and finalized the manuscript. The first draft of the manuscript was written by C.Z. (Chunyang Zhang) and S.B. (Chunyang Zhang) and S.B. performed all the electrochemical measurements and recorded the X.R.D. data. G.C. provided SEM/EDS images and analysis. M.B. and S.H. provided X.P.S. data and analysis. All authors reviewed and commented on the manuscript.

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