

Energy, Environmental, and Catalysis Applications

A Highly-Efficient and Stable Catalyst based on $\text{Co(OH)}_2@Ni$ Electroplated on Cu-Metallized Cotton Textile for Water Splitting

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48 KEYWORDS: α -Co(OH)₂; Hydrogen Evolution Reaction; Oxygen Evolution Reaction;
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50 Bifunctional Catalyst; Water Electrolysis.
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3 ABSTRACT: The concept of using renewable energy to power water electrolyzers is seen as a
4 favorable approach for the production of green and sustainable hydrogen. The electrochemical
5 water splitting can be significantly and efficiently enhanced by using bifunctional catalysts,
6 active towards both the OER (oxygen evolution reaction) and the HER (hydrogen evolution
7 reaction). Herein, a stable and highly performing catalyst based upon hybrid metal/metal
8 hydroxide nanosheet arrays electroplated onto Cu-metallized cotton textile (Co(OH)₂@Ni) was
9 designed and fabricated as a bifunctional electrocatalyst for the complete water splitting
10 reactions. It was found that the interconnected α -Co(OH)₂ nanosheets were evenly formed onto
11 the metalized cotton textile, and the optimized Co(OH)₂@Ni sample exhibited an overpotential
12 of +96 mV at 10 mA cm⁻², with excellent stability towards the HER. The *as*-prepared catalyst
13 also showed superior electrochemical activity and durability towards the OER, which was found
14 to be comparable to conventional precious group metal (PGM)-based catalysts. In addition, when
15 Co(OH)₂@Ni were assembled as the electrodes in a water electrolyzer (1 M KOH), a cell voltage
16 of 1.640 V was achieved at a current density of 10 mA cm⁻², enabling it to be a promising
17 bifunctional catalyst for water electrolysis in real applications.
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39 1. INTRODUCTION

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42 Hydrogen from water electrolyzers is now seen as an encouraging energy carrier for stationary
43 and mobile applications; and when used in a fuel cell, it only produces water.¹⁻⁴ Thus, it is a
44 renewable and practically infinite resource. During water electrolysis, the key processes are a
45 series of electrocatalytic reactions, namely the OER (oxygen evolution reaction) occurring at the
46 anode and the HER (hydrogen evolution reaction) occurring on the cathode.⁵⁻⁷ However,
47 expensive precious group metal (PGM) catalysts are usually used as catalyst materials for the
48 HER and OER due to their low anodic and cathodic overpotentials ($\eta_{a,c}$), which seriously hinders
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3 the practical application of water electrolysis.⁸⁻⁹ Over the last decade, the strategy for replacing
4 PGM catalysts by non-precious metal ones (NMPC) materials has been a dynamic research topic
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6 in the area of hydrogen and fuel cells.¹⁰⁻¹¹
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10 Transitional-metal-based catalysts, for example, sulphides,¹²⁻¹³ hydroxides,¹⁴⁻¹⁵ selenides,¹⁶⁻¹⁷
11 have been intensively investigated as encouraging substitutes to noble metal OER and HER
12 electrocatalysts. It has been shown that the development of binary transitional metal-based
13 materials, such as metal/alloy materials and metal oxides/hydroxides, could further improve the
14 electrochemical performance for water splitting due to the synergistic effect.¹⁸⁻¹⁹ For example, it
15 has been recently demonstrated that Ni(OH)₂/Ni₃S₂ nanosheets exhibited remarkable improved
16 OER and HER activities of low overpotentials i.e. +270 mV and +211 mV at a current density of
17 20 mA cm⁻², respectively.¹⁵ Although great advances have been made in the generation of
18 transitional metal-based catalyst materials, their performance is still not comparable to that of
19 PGM catalysts.
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33 To greatly enhance the electrochemical properties of transitional metal-based catalysts, the
34 microstructure of the catalysts could be re-engineered and tuned, since it has a significant impact
35 on the mass and charge transfer during the electrocatalytic processes.^{10, 20-21} At present, the
36 electrode material of integrated architecture, i.e. in which the active component with an array
37 characteristic is uniformly distributed on a three-dimensionally porous current collector without
38 binder, is thought to be a promising catalyst for water electrolysis.^{2, 22-23} In such a structure, the
39 interface/chemical distribution is homogeneous at the nanoscale and a fast ion and electron
40 transfer is guaranteed. For example, CoNiSe₂ hetero-nanorods decorated with LDH (layered
41 double hydroxide) nanosheets are produced on nickel foam to form a bind-free three-dimensional
42 electrode; in this configuration the selenide-LDHs interfaces may be able to enhance the
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3 chemisorption of water to generate reactive H intermediate, yielding in rapid hydrogen evolution
4 reaction kinetics.²⁴ So far, most of the works in the area of water electrolysis are related to these
5 materials using nickel foam and carbon materials as conductive matrices. The hydrophobicity of
6 these two materials is detrimental to the electrocatalytic process. Cotton fibers are highly
7 hydrophilic and can absorb a large amount of water or other polar solvents.²⁵ By coating a
8 conductive layer on its surface, cotton textile could be used as current collector.²⁶ Thus, the
9 electrode materials of integrated structures deposited on conductive cotton textile might result in
10 high electrocatalytic performance for water electrolysis.

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12 In this study, an approach for producing a novel hybrid metal/metal hydroxide nanosheet
13 arrays on Cu-metallized cotton textile was developed as dual-functional electrocatalyst for the
14 generation of oxygen and hydrogen. This unique structure has the following advantages: firstly,
15 it includes nickel (Ni), which endows the catalyst with good conductivity, and Co(OH)₂ can
16 chemisorb the H₂O molecular and facilitate the catalytic process; secondly, the open structure of
17 Co(OH)₂ nanosheets can make the underlying Ni layer accessible to the electrolyte and the Ni
18 layer is directly in contact with the current collector to ensure fast electron transfer; thirdly,
19 cotton has hierarchical structures possessing high surface areas, large porosity, and hydrophilic
20 functional groups. Such specific structures can boost the specific surfaces of the active materials
21 and allow the electrodes to be well-wetted by an aqueous electrolyte. The results show that the
22 optimized sample (Ni-Co-30) developed in this investigation exhibited high HER
23 electrochemical reactivity. For example, the overpotential and Tafel slope values for the
24 hydrogen evolution reaction were found to be +96 mV (at a current density of 10 mA cm⁻²)
25 and 104.2 mV dec⁻¹ respectively. The sample (Ni-Co-30) also showed higher OER
26 performance i.e. the overpotential and Tafel slope values were found to be +300 mV (at
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3 10 mA cm⁻²) and 70.1 mV dec⁻¹ respectively. Moreover, it is further demonstrated that the
4 Ni-Co-30 employed as cathode and anode in H₂O electrolysis can deliver 10 mA cm⁻² at
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6 1.640 V with greatly improved stability.
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10 **2. EXPERIMENTAL METHODS**

11 *2.1 Material Synthesis*

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16 In this study, all analytical grade (AR) chemicals were employed without any further
17 purification. Before sputtering copper (Cu) on the surface of the textile substrate, a piece of
18 cotton cloth with a size of 10 × 10 cm² (thickness: 0.36 mm) was ultrasonically clean in ethanol
19 and ultrapure water sequentially, and then dried at 60 °C in a vacuum oven. After that, both sides
20 of the cotton cloth sample were sputtered with Cu using 99.99% of pure copper as a target,
21 which was labeled as “Cu”. Subsequently, the nickel (Ni) layer was electroplated onto the
22 obtained cloth in a two-electrode electrochemical cell. In this cell, a pure Ni metal and a Cu
23 sputtered cloth was used as the positive and the negative electrodes respectively. A solution
24 containing NiSO₄ (300 g/L), NiCl₂ (45 g/L), H₃BO₃ (35 g/L) and sodium dodecyl sulfate (SDS,
25 0.05 g/L) was used to electroplate Ni onto the cloth. During the electroplating step, a constant
26 current of 10 mA cm⁻² was applied to the electrochemical cell for 30 min. After that, the obtained
27 cloth was rinsed in pure water and ethanol alternatively, and then dried at 60 °C in a vacuum
28 oven. The obtained cloth was labeled as “Ni-Cu”.
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47 Before Co(OH)₂ was electrodeposited onto the surface of Ni-Cu, the Ni-Cu was washed with
48 pure ethanol and ultrapure water. The electrolyte used for electrodeposition was 0.05 M
49 Co(NO₃)₂. The electrodeposition experiments were performed out in a 3-electrode
50 electrochemical cell by cyclic voltammetry for 30 cycles over a potential range of -1.2 to -0.8 V
51 vs. Ag/AgCl at a scan rate of 50 mV s⁻¹. In this electrochemical cell, the cleaned “Ni-Cu” sample
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3 was employed as the WE (working electrode), Pt as CE (counter electrode) and Ag/AgCl as RE
4 (reference electrode). After electrodeposition, the obtained electrode was washed with pure water
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6 and then dried in a vacuum oven for 12 hours. The *as*-prepared electrode was labeled as “Ni-Co-
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X” (X: CV cycling number).

2.2 Physical Characterization

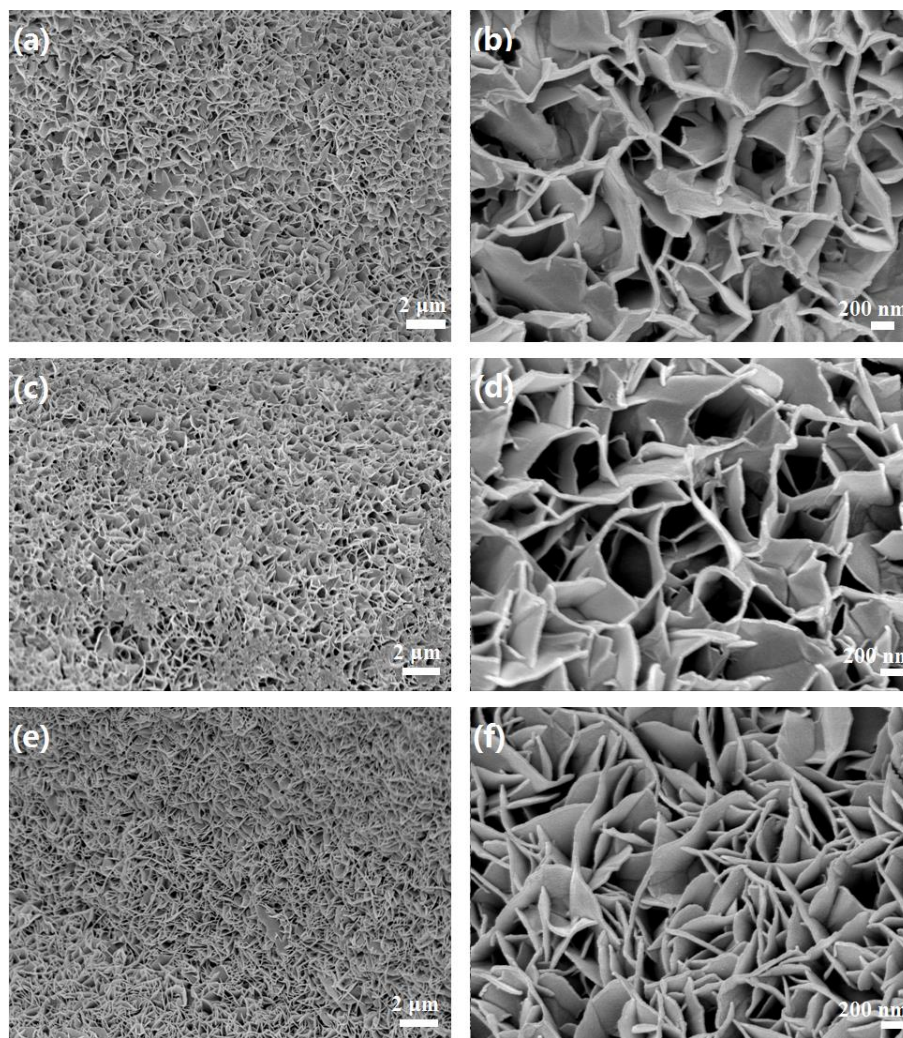
XRD (X-ray diffraction) spectra of the *as*-prepared catalysts were generated on a Shimadzu XD-3A (Japan), using filtered Cu-K α radiation ($\lambda = 0.15418$ nm), generated at 40 kV and 30 mA. Scans for 2θ values were recorded at 5° min^{-1} between 10° and 80° . SEM (scanning electron microscopy) images were obtained using a Carl Zeiss Ultra Plus electron microscope. Scans for 2θ values were recorded at 4° min^{-1} between 10° and 80° . TEM (Transmission electron microscopy) images were taken on a JEOL (JEM-2000 FX) microscope operating at 200 kV. XPS (X-ray photoelectron) spectra were generated using a VG Escalab210 spectrometer fitted with Mg 300 W X-ray source.

2.3 Electrochemical Characterization

The HER and OER electrochemical performances were evaluated in a 3-electrode electrochemical cell connected to a potentiostat/galvanostat (CHI 660, CH Instruments, Inc., Shanghai). During the testing, the reference electrode (RE) and counter electrode (CE) was a Hg/HgO and a graphite rod respectively. LSV (linear sweep voltammetry) and CV (cyclic voltammetry) voltammograms were performed in a 1.0 M potassium hydroxide (KOH) electrolyte. EIS (Electrochemical impedance spectroscopy) spectra were measured at corresponding OER and HER electrode potentials from 0.01 to 1,000,000 Hz with an amplitude of 5 mV. To evaluate the “Ni-Co-X” performance in the overall water splitting, “Ni-Co-X”

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3 was used as cathode and anode in a 2-electrode cell configuration. LSV voltammograms
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5 were recorded at a scan rate of 5 mV s^{-1} . All potentials stated in this study, are referenced to a
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7 RHE (reversible hydrogen electrode). iR compensation (90%) was used for all electrochemical
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9 experiments.
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11 12 13 3. RESULTS AND DISCUSSION 14



48
49 **Figure 1.** SEM pictures of Ni-Co-Cu electrodes synthesized under various CV cycles (a,b) Ni-
50 Co-20; (c,d) Ni-Co-30; (e,f) Ni-Co-40.
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3 In this study, a novel cotton-based material was developed to support Co(OH)_2 nanosheets as
4 water splitting electrocatalyst material having dual functionality. Firstly, cotton was sputtered
5 with copper (Cu) onto its surface to make cotton electrically conductive. After that, the cotton-
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8 Cu sample was electrochemically coated with nickel (Ni) on its surface to improve the electrical
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10 conductivity and electrochemical stability. Subsequently, the Co(OH)_2 layer was
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12 electrodeposited on the surface of Ni-Cu via cyclic voltammetry. Figure S1 shows the color of
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14 the blank cotton textile, Cu-metalized cotton, Ni-coated cotton, and $\text{Co(OH)}_2@$ Ni. The
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16 morphology of the “Ni-Co-X” samples synthesized via cyclic voltammetry was evaluated by
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18 scanning electron microscopy (SEM). As represented in Figure 1(a, c and e), interconnected
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20 Co(OH)_2 nanosheets were evenly formed onto the surface of “Ni-Cu”. There is no obvious
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22 change of the sheet-like morphology when electrochemical deposition occurred in the range of
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24 20 to 40 CV cycles. As presented in the zoomed SEM images in Figure 1(b, d, and f), the
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26 Co(OH)_2 nanosheets became denser with an increased number of CV cycles. These figures also
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28 show that Co(OH)_2 nanosheets of the three samples were interconnected with each other,
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30 forming a three-dimensional configuration with an open structure. In such a structure, the more
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32 exposed surface is in contact with the electrolyte, which can in turn efficiently facilitates the ion
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34 and electron transfer during the electrochemical processes.²⁹⁻³⁰
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42 The crystal phase of the *as*-prepared Ni-Co-30 was investigated by XRD. As presented in
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44 Figure 2(a), characteristic diffraction peaks of Ni at 44.6° , 51.8° and 76.6° corresponding to the
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46 (111), (200), and (220) planes of the face-centered cubic Ni (JCPDS No.70-0809) and Cu at
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48 43.34° , 50.46° and 74.18° related to the (111), (200), and (220) planes of the face-centered cubic
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50 Cu (JCPDS No.70-3039), were observed in the XRD pattern of Ni-Co-30. These characteristic
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52 peaks of α - Co(OH)_2 according to the JCPDS No.46-0605 are clearly shown in the XRD pattern
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3 over the range of 10 - 60°. The intensities of the peaks of Co(OH)₂, compared to those of Ni and
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5 Cu, are low, indicating that the Co(OH)₂ nanosheets with low crystallinity were formed onto the
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7 Ni-Co-30. α -Co(OH)₂ possesses a hydroxalcalite-like structure containing positively charged
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9 Co(OH)_{2-x}(OH)_x layers as well as balancing anions accumulated between the hydroxide layers.
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11 Due to its larger interlayer spacing, this type of material has been shown to be better than β -
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13 Co(OH)₂ in terms of electrochemical activities.³¹ In addition, the peak of (003) plane is much
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15 higher than the others, implying that the Co(OH)₂ crystal is preferred to form along the (003)
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17 plane direction with larger interlayer space than the other planes. These larger interlayer spaces
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19 are able to accumulate more electrolyte ion and improve the contact between the electrolyte and
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21 the electrode.
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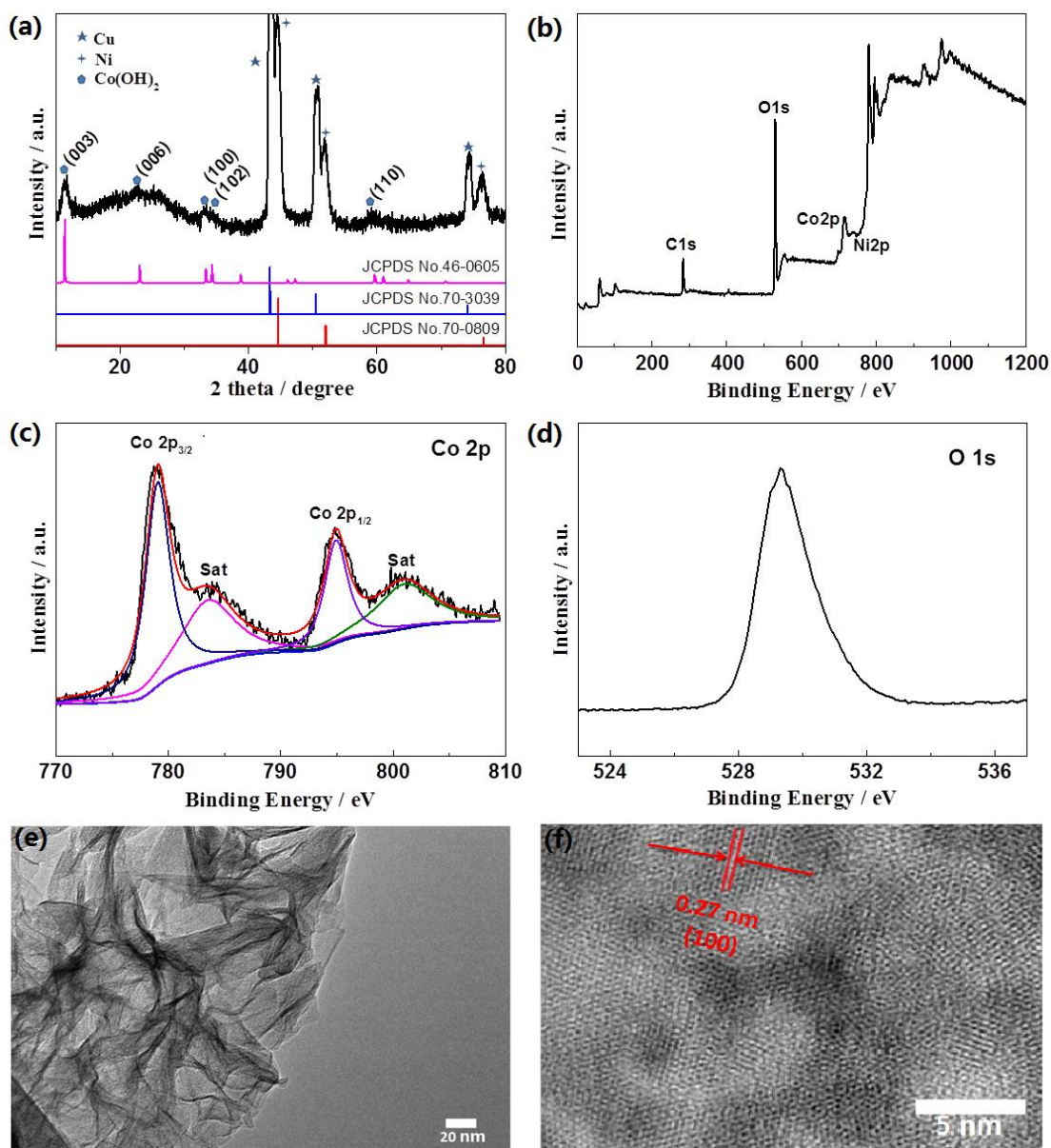


Figure 2. (a) XRD pattern of Ni-Co-30; (b) Survey XPS spectrum of Ni-Co-30; (c,d) The deconvoluted HR XPS spectra of Co $2p$ (c) and O $1s$; (d) for Ni-Co-30 electrode; (e) TEM image and (f) HR TEM image of Ni-Co-30.

XPS analyses were performed to probe the Ni-Co-30 chemical state and surface composition as presented in Figure 2(b-d). Figure 2(b) shows the presence of C $1s$, Ni $2p$, O $1s$ and Co $2p$ in the Ni-Co-30. The signal for Cu was not observed since the XPS can only detect the elements

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3 which are close to the surface (within a range of 4 nm),³² indicating that the Cu layer was fully
4 covered with Ni and Co(OH)₂. Figure 2(b) also shows that the intensity of Co peak is much
5 higher than that of Ni, indicating that Ni layer was further covered by Co(OH)₂. The XPS signal
6 of Co 2p may be fitted into 4 peaks at 783.5 eV, 801.0 eV, 779.1 eV, and 794.9 eV,
7 corresponding to two spin-orbit doublet, i.e. Co 2p_{3/2} and Co 2p_{1/2}, as well as 2 shake-up
8 satellites, indicating the existence of Co with oxidation state in Ni-Co.³³⁻³⁴ The binding energy at
9 869.9 eV indicates that only Co oxide existed on the surface of Ni-Co-30.³⁵

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TEM analyses were further performed to study the morphology of the Ni-Co-30. The TEM image (Figure 2(e)) shows that Co(OH)₂ nanosheets possess rough surfaces, on which many wrinkles and grain boundaries may be seen. Figure 2(f) shows a HR TEM image, and well-defined lattice fringes with a *d*-spacing distance of 0.27 nm corresponding to (100) crystalline plane of α-Co(OH)₂ can be observed, further confirming that α-Co(OH)₂ covered the surface of the Ni-Co-30.

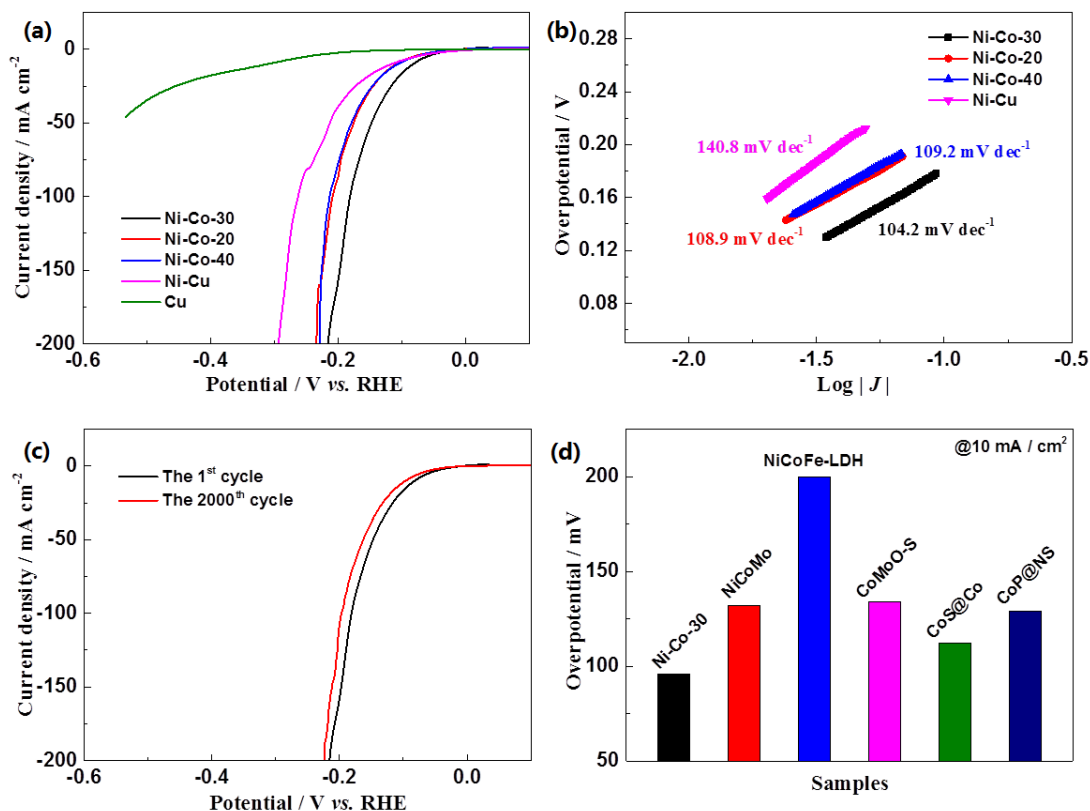


Figure 3. HER electrocatalytic measurements in 1.0 M KOH. (a) LSV voltammogram; (b) Tafel plots; (c) HER LSV curves for the 1st and 2,000th cycles; (d) Overpotentials comparison for all samples at $j = 10 \text{ mA cm}^{-2}$.

The hydrogen evolution reaction electrocatalytic activity of “Ni-Cu” and “Ni-Co-X” synthesized with various CV cycles were evaluated in 1.0 M potassium hydroxide (KOH). As presented in Figure 3(a), the Cu sample exhibits poor activity towards the HER. After Ni was deposited, the Ni-Cu became active towards the HER, indicating that Ni layer is active for HER. The onset potentials of Ni-Cu, Ni-Co-20, Ni-Co-30, Ni-Co-40 were -140 mV, -122 mV, -96 mV and -124 mV (*vs.* RHE) respectively. The onset potentials of all Ni-Co samples were more negative than that of the Cu-Ni sample, implying that the Co(OH)_2 layer had a crucial role in enhancing the HER activity. For the Ni-Co-30 sample, a HER overpotential was found to be +96

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3 mV (at 10 mA cm^{-2}), a value which was lower than all the other samples, in other words, Ni-Co-
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5 30 exhibited the highest HER activity among all tested samples. The overpotentials of all “Ni-
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7 Co-X” samples were lower than +150 mV, making them useable for practical water splitting
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9 applications. To further shed light on the HER process occurring on these electrodes, Tafel plots
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11 were generated (Figure 3(b)) from the polarization curves shown in Figure 3(a). Three steps are
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13 involved in the HER process, namely *Volmer*, *Heyrovsky* and *Tafel* steps.³⁶ In our conditions, the
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15 hydrogen evolution reaction occurring on the “Ni-Co-X” electrodes went through the *Volmer*-
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17 *Heyrovsky* step, in which the HER *rds* (rate determining step) is the electrochemical desorption.
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19 The HER overpotential (at 10 mA cm^{-2}) for the Ni-Co-30 sample was also compared with some
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21 representative Co-based electrocatalysts previously reported in other studies (shown in Table S1
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23 and Figure 3(d)), which clearly highlights that Ni-Co-30 is one of the best catalysts among them
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25 in terms of low overpotential (i.e. +96 mV).
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31 Durability is another critical parameter when developing and evaluating electrocatalysts for
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33 water splitting. The durability experiments were conducted by CV for 2,000 cycles in 1.0 M
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35 KOH electrolyte. The 1st and the 2,000th cycles LSV curves of Ni-Co-30 and “best” and
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37 commercial hydrogen evolution reaction catalyst, Pt/C, are presented in Figure 3(c) and Figure
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39 S2(a). After the durability experiments, the overpotential of Ni-Co-30 shifted by +12 mV, which
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41 was lower than the overpotential shift of + 32 mV for Pt/C.
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45 Although the SEM results show that the three “Ni-Co-X” samples have similar morphologies,
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47 the Co(OH)_2 nanosheet densities are slightly different, which could result in different effective
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49 surface areas formed on the “Ni-Co-X”. To assess the effective surface area, the CV method was
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51 employed to quantify the electrochemical double-layer capacitance for these “Ni-Co-X” samples
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53 based upon reported methods.⁶ A potential window from 0.46 to 0.56 V for the CV experiment
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3 was carefully chosen to avoid any involvement of *Faradaic* currents. Their corresponding CV
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5 voltammograms at various scan rates are presented in Figure S3. The obtained corresponding
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7 capacitance values are presented in Figure S4(a), indicating that the Ni-Co-30 sample has the
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9 highest capacitance among all four samples, namely the CV cycle number for depositing
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11 Co(OH)_2 has a significant impact on the effective surface area. Moreover, it appears that there is
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13 an optimized CV cycle number for growing Co(OH)_2 nanosheets onto the Ni layer surface. For
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15 example, when the CV cycle number is low, not enough Co(OH)_2 nanosheets are formed onto
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17 the Ni layer. However, when the CV cycle number is too high, the Co(OH)_2 nanosheets formed
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19 on the Ni layer could be too dense, in turns making some nanosheets inaccessible for the
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21 electrolyte during the electrochemical processes. The electrode kinetics were further studied by
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23 EIS (electrochemical impedance spectroscopy) under these conditions. *Nyquist* plots at high-
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25 frequency ranges were found to be of semi-circles (Figure S4b), relating to the charge-transfer
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27 resistance (R_{ct}). The R_{ct} of Ni-Co-30 was found to be the lowest among all the samples. The EIS
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29 result revealed that the Co(OH)_2 nanosheets formed after 30 CV cycles could bring more
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31 exposed surface area in contact with the electrolyte, resulting in a better charge-transfer during
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33 the HER. In this investigation, the authors used the same technique to electrodeposit on the
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35 surface of Ni foam (NF) and Carbon fiber cloth (CF). The performance of the Ni-Co-30 sample
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37 was obviously better than that of CF-30 and NF-30 (Figure S4c).
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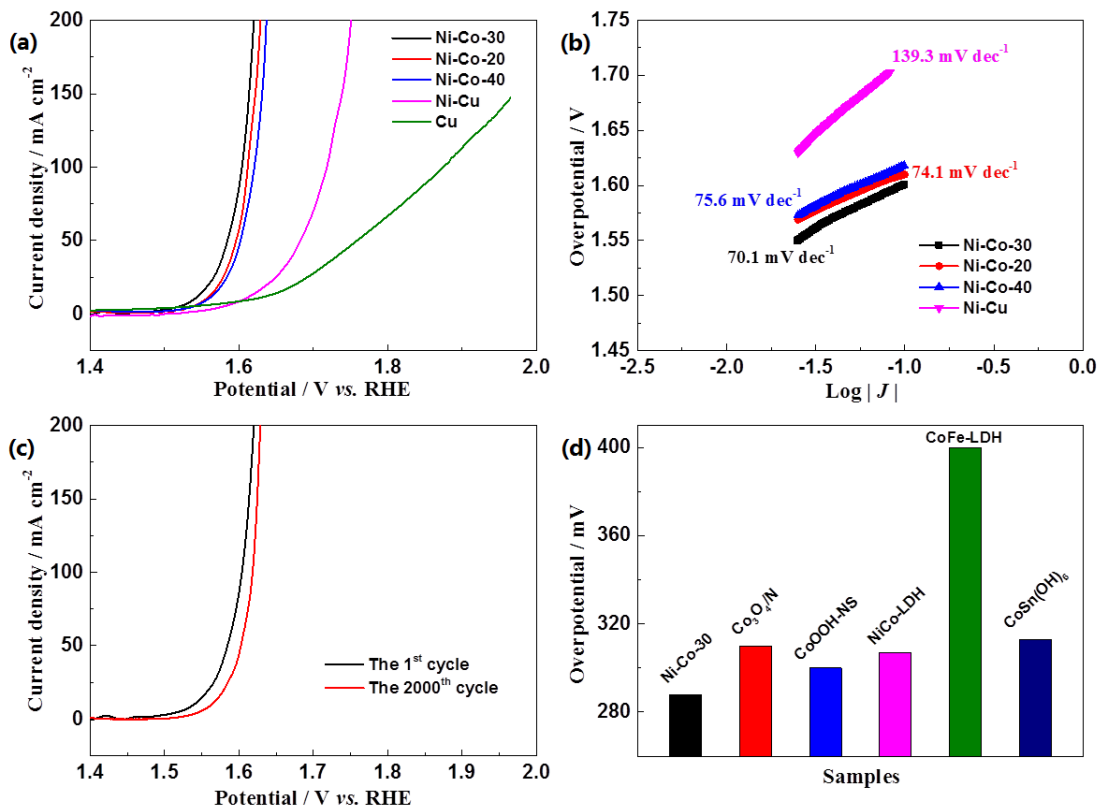


Figure 4. OER electrocatalytic measurements in 1.0 M KOH. (a) LSV curves; (b) Tafel plots; (c) OER LSV curves for the 1st and the 2,000th cycles; (d) Overpotentials comparison at $j = 10 \text{ mA cm}^{-2}$ for all samples.

The OER activity for Ni and “Ni-Co-X” samples was further investigated in a 1.0 M KOH electrolyte by LSV (scan rate of 5 mV s^{-1}). The obtained LSV voltammograms are presented in Figure 4(a). It may be observed from the figure that the Cu sample exhibits poor activity towards OER, and a relatively good OER activity can be achieved after Ni was deposited. The three “Ni-Co-X” samples are more active towards the OER than Cu and Cu-Ni, especially the Ni-Co-30 sample. The OER onset potential for the Ni-Co-30 sample was similar to that of the “best” OER RuO₂ catalyst reported by Wang *et al.*,⁹ in other words, the OER activity of Ni-Co-30 is comparable to that of RuO₂. Tafel plots were also produced to evaluate the samples OER kinetics. Their corresponding Tafel slopes are shown in Figure 4(b), showing that the Ni-Co-30

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3 catalyst has the lowest Tafel slope, indicating that Ni-Co-30 has a better OER kinetics than the
4 other three materials. Since the rapid charge-transfer kinetics usually results in high OER
5 electrocatalytic performance, EIS (electrochemical impedance spectroscopy) was performed on
6 these electrodes under OER operating conditions. *Nyquist* plot at high-frequency range indicates
7 that electrode kinetics charge-transfer resistance. As shown in Figure S5, Ni-Co-30 exhibited the
8 lowest resistance in the OER, implying that the charge-transfer on Ni-Co-30 was better than the
9 other three samples.
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20 Durability experiments of Ni-Co-30 and RuO₂ catalysts were conducted by continuous OER
21 CV for 2,000 cycles in 1.0 M KOH. The Ni-Co-30 catalyst OER onset potential changed from
22 +1.530 to +1.551 V vs. RHE, i.e. slightly increased by +21 mV after durability testing. This shift
23 of onset potential for the RuO₂ catalyst was found to be +45 mV after the 2,000th LSV cycle
24 (Figure S2(b)). The OER durability testing showed that the Ni-Co-30 catalyst had an excellent
25 stability towards the OER in an alkaline electrolyte. The OER overpotential (at 10 mA cm⁻²) for
26 the Ni-Co-30 catalyst was benchmarked against those of several other Co-based OER catalysts
27 as shown in Figure 4(d) and Table S2, indicating that the Ni-Co-30 catalyst is a very hopeful
28 OER non-noble metal electrocatalysts among other OER catalysts previously reported in the
29 literature.
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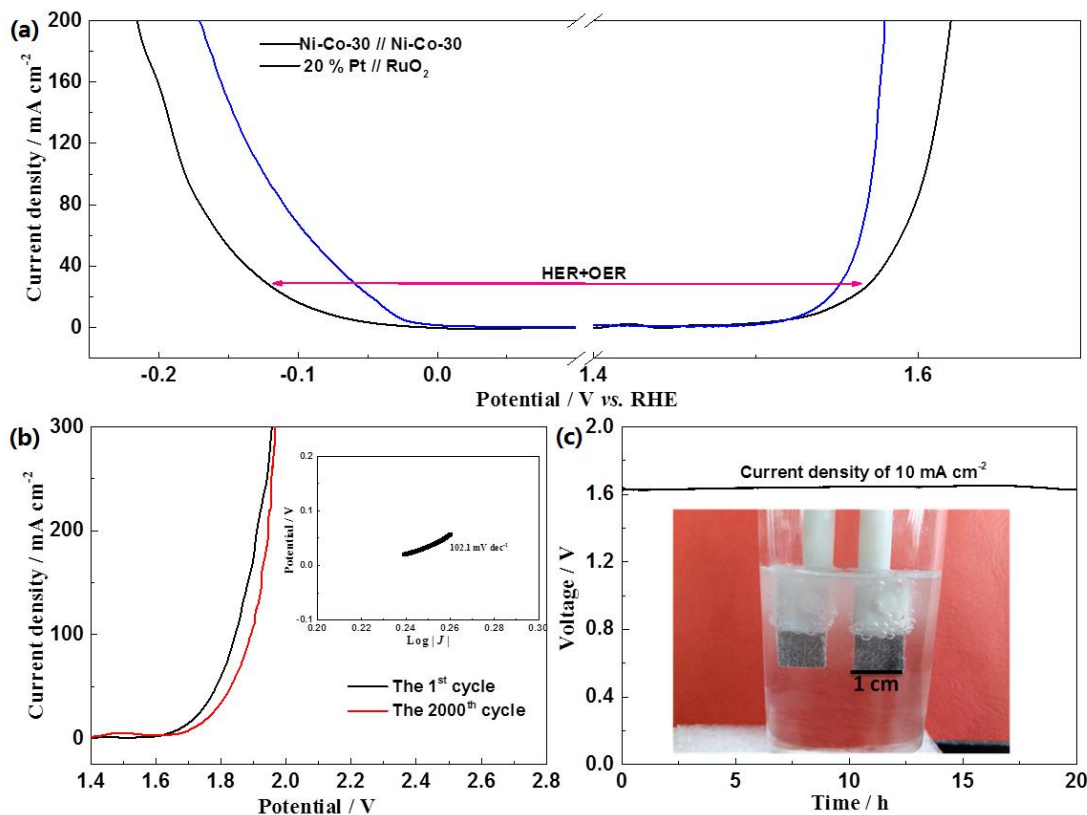


Figure 5. Electrocatalytic measurements for overall water splitting in 1.0 M KOH. (a) Linear sweep voltammogram for HER and OER; (b) Polarization curves of the hierarchical $\text{Co}(\text{OH})_2$ nanosheets for overall water splitting and Tafel plots for Ni-Co-30; (c) Chronopotentiometry analyses in a 2-electrode set up at a constant current density (10 mA cm^{-2}) were performed and a picture of the overall water splitting cell.

To evaluate the performance of the hydrogen and oxygen evolution reactions of the Ni-Co-30 catalyst in “real” water electrolysis conditions, the Ni-Co-30 catalyst was used as both the anode and the cathode in 1 M KOH in a two-electrode cell (Ni-Co-30||Ni-Co-30 electrolyzer). The hydrogen and oxygen evolution reaction polarization curves are shown in Figure 5(a). A cell voltage of 1.640 V was achieved at 10 mA cm^{-2} . Although the cell voltage was still higher than that observed for Pt/C||RuO₂ (Ni foam) (1.558 V), Table S3 shows that our reported cell voltage is much lower than many others reported Co-based water electrolyzers. The durability of the Ni-

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3 Co catalyst for the overall water splitting was further evaluated by 2,000 continuous cycles. The
4 corresponding LSVs for the 1st and 2,000th cycles are shown in Figure 5(b). After cycling, the cell
5 voltage increased by +15 mV (i.e. from 1.640 V to 1.655 V). For comparison purposes,
6 durability experiments were also performed on the Pt/C||RuO₂ (Ni foam) cell. The cell voltage
7 for Pt/C||RuO₂ (Ni foam) increased by +36 mV (Figure S2(c)), a value which is much higher
8 than that of Ni-Co-30||Ni-Co-30 cell; therefore in our conditions, the Ni-Co-30 catalyst showed
9 better durability than RuO₂ and Pt/C for the complete water splitting electrochemical reactions.
10 Moreover, in the durability study (Figure 5(c)) carried out by continuous electrolysis at a
11 constant current density (10 mA cm⁻²), a cell voltage of ca. 1.640 V was stable for over 20 hours
12 of operation with negligible degradation. The Ni-Co-30 catalyst morphology was also retained as
13 shown in Figure S6. A picture of the Ni-Co-30||Ni-Co-30 electrolyzer cell is shown in Figure
14 5(c), in which H₂ and O₂ gas bubbles were generated on both electrodes, further indicating the
15 highly electrocatalytic activity of the Ni-Co-30 catalyst.
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34 4. CONCLUSIONS

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36 A novel structured Co(OH)₂ nanosheet material was successfully electrodeposited onto a Ni-
37 coated metalized cotton textile to form a hybrid of metal/metal hydroxide electrocatalyst for the
38 HER and the OER. The Ni-Co-30 exhibited high HER and OER electrocatalytic activities with
39 excellent durability, which in some cases, outclassed most of the Co-based HER and OER
40 catalysts reported other investigations. Its oxygen evolution performance was comparable to that
41 of the “best” RuO₂ catalyst. Moreover, the Ni-Co-30 electrodes were assembled as cathode and
42 anode in a “real” water electrolyzer in the presence of 1.0 M KOH. The assembled electrolyzer
43 produced a cell voltage of 1.640 V at a current density of 10 mA cm⁻². The Ni-Co-30 electrodes
44 exhibited better durability than that of the Pt/C||RuO₂ used for water electrolysis. This
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3 investigation highlighted that the hybrid α -Co(OH)₂@Ni could be an encouraging transitional
4 metal electrode material employed as an electrocatalyst for both the hydrogen and oxygen
5 evolution reactions.
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10 ASSOCIATED CONTENT

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14 Determined double-layer capacitance, Electrochemical impedance spectroscopy, SEM pictures
15 of Co-Ni-30 after stability test are in Supporting Information.
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35 **Author Contributions**

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37 The manuscript was written through contributions of all authors. All authors have given approval
38 to the final version of the manuscript.
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42 **Notes**

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46 The authors declare no competing financial interest.
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Graphical abstract

