Nanosheets of NiCo$_2$O$_4$/NiO as Efficient and Stable Electrocatalyst for Oxygen Evolution Reaction

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ABSTRACT: Development of a stable catalyst that can efficiently function for longer time for energy conversion process in water splitting is a challenging work. Here, NiCo$_2$O$_4$/NiO nanosheets are successfully synthesized following a simple wet-chemical route, followed by the combustion technique. Finally, the synthesized catalyst NiCo$_2$O$_4$/NiO can function as an efficient catalyst for oxygen evolution reaction. Nanosheets with interconnections are very useful for better electron transportation because the pores in between the sheets are useful for the diffusion of electrolyte in electrocatalysis. In oxygen evolution reaction, these sheets can generate current densities of 10 and 20 mA/cm$^2$, respectively, upon application of 1.59 and 1.62 V potential versus reversible hydrogen electrode (RHE) under alkaline condition. In contrast, bare NiCo$_2$O$_4$ nanowire bundles can generate a current density of 10 mA/cm$^2$ upon application of 1.66 V versus RHE. The presence of NiO in NiCo$_2$O$_4$/NiO nanosheets helps to increase the conductivity, which further increases the electrocatalytic activity of NiCo$_2$O$_4$/NiO nanosheets.

1. INTRODUCTION

Most important and immerging challenge is to find “green” and “renewable” energy resources due to the inadequate availability of fossil fuel and day-to-day increasing energy demand for everyday life, and at the same time, conventional energy sources have many environmental emission issues. Water splitting has attracted great interest in recent years because only by application of current it can generate hydrogen and oxygen. Hydrogen resulting from the production of electricity from renewable sources, such as solar or wind, will have advantages from emissions benefits. On earth, it is unlikely to transpire hydrogen naturally in large quantities. For the industrial production of hydrogen, substantial amount of energy is required. Solar water splitting for the production of hydrogen as an energy carrier using only water and sunlight on the earth is extremely attractive. A large overpotential of oxygen evolution reaction (OER) restricts the practical application of water splitting. The important challenge for oxygen production is to unveil a way by which the cost of production technologies can be minimized and it can be commercialized. Precious metals are efficient catalysts for oxygen evolution reaction (OER) and hydrogen evolution reaction (HER), but their practical ability is bounded because of the low availability, high cost, and stability issue. Precious metal oxides like RuO$_2$ and IrO$_2$ are studied as efficient OER and Pt as HER catalyst having low onset potential. It is obvious to design an effective and economical catalyst using non-noble metals, which can function as an efficient OER or HER catalyst with high durability.

Metal oxides of Mn, Cu, Ni, Co, and Fe are developed and frequently studied for their OER activity. Cobalt-based oxides are most promising electrocatalysts because of their high abundance, easy preparation, and stability. Metal-doped Co$_3$O$_4$ shows improved electrocatalytic activity compared to bare Co$_3$O$_4$. Among these non-noble-metal-based catalysts, NiCo$_2$O$_4$ has received considerable attention in oxygen evolution reaction because of its better electronic and ionic conductivity, low cost, stability, and so forth. In NiCo$_2$O$_4$, the octahedral sites are filled with nickel, and cobalt occupies both the octahedral and tetrahedral sites. Redox chemistry of NiCo$_2$O$_4$ is rich because of the dual contribution of nickel and cobalt. Recent studies have demonstrated that NiCo$_2$O$_4$ has excellent electrochemical activity and electronic conductivity, which are always higher than those of the counter monometallic oxides (NiO and Co$_3$O$_4$). Different morphologies of NiCo$_2$O$_4$ were extensively studied for its OER activity. Xiao et al. reported the synthesis of NiCo$_2$O$_4$ nanosheets, which can generate a current density of 10 mA/cm$^2$ upon application of 1.63 V potential versus reversible hydrogen electrode (RHE) under 1 M KOH condition. The electrocatalytic activity of NiCo$_2$O$_4$ nanosheets decorated on CNTs, which is much higher than that of bare NiCo$_2$O$_4$, was reported by Chen et al.

Yan et al. reported that Fe-doped NiCo$_2$O$_4$ shows higher electrocatalytic activity compared to NiCo$_2$O$_4$ in 1 M KOH. Bare NiCo$_2$O$_4$ requires 1.69 V to generate a current density of 10 mA/cm$^2$ with a Tafel slope of 75 mV/decade.

Sheet like structure with high active surface atoms can function as efficient catalyst for OER reaction. Umeshbabu et al. exhibited enhanced electrocatalytic activity for OER and methanol oxidation when NiCo$_2$O$_4$ hexagonal plates were attached to reduced graphene oxide sheets, with high surface...
Xia et al. reported Au−NiCo2O4 supported on a graphene-like sheet, where the latter is introduced as a conductive support to increase the specific area and helps to improve the conductivity of NiCo2O4. Similarly, NiCo2O4 nanosponges exhibited excellent electrocatalytic activity for OER reaction, as shown by Zhu et al. Motivated by previous studies, in the present report, two-dimensional (2D) sheets of NiCo2O4/NiO are synthesized using a wet-chemical route, followed by calcination technique. The structure, composition, and surface morphology were characterized by X-ray diffraction (XRD), Raman spectroscopy, scanning/transmission electron microscopy (SEM/TEM), and X-ray photoelectron spectroscopy (XPS) analyses. NiCo2O4/NiO sheets can function as efficient catalyst for OER reaction under alkaline condition. In oxygen evolution reaction, NiCo2O4/NiO sheets can generate a current density of 10 mA/cm² upon application of 1.59 V potential versus RHE. It was found that NiCo2O4/NiO sheets can outperform commercial RuO2, exhibiting a small potential of 1.59 V at a current density of 10 mA/cm² and a small Tafel value of 61 mV/decade during OER in 1 M NaOH.

2. RESULTS AND DISCUSSION

2.1. Synthesis. For the synthesis of NiCo2O4/NiO sheets, 2.0 mL of NiCl2 (0.1 mol/L) and 4 mL of Co(NO3)2 (0.1 mol/L) solutions were mixed together with certain amount of urea and glucose. The mixture was stirred and heated at 140 °C for 6 h, followed by calcination at 500 °C for 15 h in air. A similar type of methodology for the synthesis of monometallic oxides was reported by Zhou et al. More details of the experimental steps are given in Experimental Section. Bare NiCo2O4 was separately synthesized via hydrothermal technique (details are given in Experimental Section). Bare NiO was also synthesized using the wet-chemical technique, followed by combustion (details are given in Experimental Section). A physical mixture of NiCo2O4 and NiO was also prepared by mixing NiCo2O4 (synthesized through hydrothermal technique) and NiO in the composition ratio 1:0.13, denoted as NiCo2O4−NiO pm throughout the MS.

2.2. Morphology and Structure. The crystal structure, composition, and phase purity of the as-synthesized material were initially characterized by powder X-ray diffraction (PXRD) analysis. Scheme 1 shows the schematic representation of the synthesis of NiCo2O4/NiO sheets, Figure 1a shows the PXRD pattern of the as-synthesized material. All peaks are well matched with the cubic NiCo2O4 (JCPDS No.: 20-0781) and cubic NiO (JCPDS No.: 73-1519). There is no unidentiﬁed peak in the XRD pattern, which again clearly demonstrates that the synthesized product is NiCo2O4 with NiO. To know the growth mechanism, time-dependent XRD was carried out. Figure S1a shows the XRD pattern of Ni−Co sample before calcination, where no characteristic peak was identiﬁed leaving aside the amorphous peak of "C". So, after heating at 140 °C for 6 h, only metal ions get embedded on spongy "C" surface. XRD was carried out at different time intervals of calcination, such as 30 min, 3, 6, 10, and 15 h, and the results are shown in Figure S1a,b. After 3 h of calcination, XRD shows the presence of NiO along with NiCo2O4. With further increase in calcination time, NiO gets converted to NiCo2O4 as the peak intensity of NiO certainly decreased on 6 h calcination. Finally, the XRD pattern of the 10 h sample clearly shows that there is only 13% NiO present in NiCo2O4. Again, calcination up to 15 h exhibits enhanced amount of NiO.
in NiCo2O4, which may be due to the decomposition of NiCo2O4 upon longer heating. So, the optimum condition for calcination is 10 h to get minimum amount of NiO on NiCo2O4. The XRD pattern of NiCo2O4 synthesized by hydrothermal method and NiO is shown in Figure S2.

The existence of NiO in NiCo2O4/NiO can be clearly identified by Raman spectroscopy. Figure 1b displays the Raman spectra of NiCo2O4/NiO, pure NiO, and NiCo2O4. In case of NiO, two main peaks are observed centered at 505 and 1074 cm\(^{-1}\), which are due to one phonon (1P) mode and two phonon (2P) modes of two longitudinal-optical (2LO), respectively. Pure NiCo2O4 shows peaks at 194, 467, 519, and 672 cm\(^{-1}\), which are due to \(F_{2-g}, E_g, LO,\) and \(A_{1-g}\) modes of NiCo2O4, respectively. The Raman spectra of NiCo2O4/NiO show peaks at 190, 467, 515, 665, and 1077 cm\(^{-1}\), which clearly demonstrate the presence of both NiO and NiCo2O4 in the as-synthesized NiCo2O4/NiO.

The morphology of the as-synthesized product was characterized by scanning electron microscopy (SEM). Figures 2a,b and S3 show the SEM images of NiCo2O4/NiO in different magnifications. The low-magnification image shows that highly dense interconnected nanosheets of NiCo2O4 are synthesized following this method. These interconnected sheets are very useful for better electron transportation because the pores in between the sheets are useful for the diffusion of electrolyte in electrocatalysis. Lengths of these sheets are in the range of micrometers, whereas widths are in nanometers. A high-magnification SEM image of NiCo2O4/NiO sheets is shown in the inset of Figure 2b, which shows that very small nanoparticles work as the building blocks to give rise to the sheet-like structure. (c) TEM image of NiCo2O4/NiO sheets, and the inset shows the high-magnification TEM image. (d) HRTEM image of NiCo2O4/NiO sheets.

Figure 2. (a, b) Field-emission SEM (FESEM) images of NiCo2O4/NiO in different magnifications: (a) low magnification and (b) medium magnification, which shows that the as-synthesized materials have the nanosheet morphology; the inset shows the high-magnification SEM image, which shows that the small particles of NiCo2O4/NiO arranged themselves to give rise to the sheet-like structure. (c) TEM image of NiCo2O4/NiO sheets, and the inset shows the high-magnification TEM image. (d) HRTEM image of NiCo2O4/NiO sheets.
O as elements. Figure S5 shows the uniform distribution of Ni, Co, and O throughout the nanosheet structure.

Transmission electron microscopy (TEM) was also used to determine the crystallinity and to recheck the morphology. Figures 2c and S6 show the TEM images of the synthesized NiCo₂O₄/NiO, which confirm the sheet like structure consistent with the SEM image. The inset of Figure 2c shows a high-magnification TEM image, which confirms that the as-synthesized nanosheets are composed of very small particles with particle size ~50 nm. HRTEM analysis (Figure 2d) shows the interplanar spacing of about 0.25 nm, which corresponds to the spacing between two (311) crystal planes of NiCo₂O₄.20 Figure S7a,b shows the TEM images (in different magnifications) of bare NiCo₂O₄ synthesized through hydrothermal method. It shows that bundles of NiCo₂O₄ nanowire were synthesized following hydrothermal technique. HRTEM analysis of NiCo₂O₄ bundles exhibits an interplanar spacing of 0.25 nm, which corresponds to the spacing of (311) plane (Figure S7c). EDS analysis shows the presence of Ni, Co, and O and their homogeneous distribution throughout the nanowire bundle (Figure S8).

To have a clear understanding on the composition and oxidation of the metals present in NiCo₂O₄/NiO, XPS was carried out, and the results are shown in Figure 3. Survey spectra are shown in Figure 3a, which shows the presence of Ni, Co, C, and O and the absence of any impurity. High-resolution spectra of Ni 2p can be fitted with two spin−orbit doublets and two shakeup satellite peaks. These two spin−orbit doublets are of Ni²⁺ and Ni³⁺, and the two shakeup satellite peaks are assigned as "sat" in Figure 3b. Specifically, peaks at binding energies of 854.5 and 872.3 eV are assigned to Ni³⁺ and other two peaks at 858.4 and 877.8 eV are of Ni⁴⁺. In a similar way, Co 2p is also fitted, the doublet peaks at binding energies of 779.1 and 794.7 eV are assigned to Co³⁺, and peaks at 780.6 and 796.6 eV are due to Co²⁺ species (Figure 3c). XPS results indicate that NiCo₂O₄/NiO contains Ni²⁺/Ni³⁺ and at the same time Co²⁺/Co³⁺. The observed XPS result is in accordance with the existing literature.21 O 1s spectra show only two contributions, which are denoted as O1 centered at 529.1 eV and O2 at 530.1 eV (Figure 3d). Specifically, the peak located at 529.1 eV is assigned due to the metal−oxygen bond. The peak at 530.1 eV is usually associated with defects and
contaminants. There is no peak beyond 531 eV, which again proves that there is no chemisorbed oxygen in the material, which is in agreement with our experimental procedure.

**2.3. Electro catalytic Activity.** The electrocatalytic activity of NiCo$_2$O$_4$/NiO was evaluated using linear sweep voltammetry (LSV). All of the electrochemical measurements for oxygen evolution reaction were carried out in 1 M NaOH solution. Figure 4 shows the polarization curve of NiCo$_2$O$_4$/NiO sheets, bare NiCo$_2$O$_4$, NiO, RuO$_2$, and bare glassy carbon (GC) electrode measured at a scan rate of 2 mV/s. Potentials are measured with respect to Ag/AgCl electrode and reported with respect to reversible hydrogen electrode. Bare GC does not show any catalytic activity in the measured potential range. If the scan rate is high, i.e., 50 mV/s, it is observed that NiCo$_2$O$_4$/NiO sheets exhibit two anodic oxidation peaks (Figure S9). The first peak is centered at 1.42 V, and the second one is at 1.55 V: the first peak is due to the oxidation of Co$^{3+}$ to Co$^{4+}$, and the second peak is due to the oxidation of water. This result is consistent with the literature. In the spinel structure, nickel is present in the octahedral site, whereas cobalt is present in both the tetrahedral and octahedral sites. During electrocatalysis, the presence of a peak at 1.42 V signifies that Co$^{3+}$ is the main active species in the NiCo$_2$O$_4$/NiO. That is why, peaks of Ni$^{2+}$ to Ni$^{3+}$ and Co$^{2+}$ to Co$^{3+}$ are missing in the LSV scan. It is noted that NiCo$_2$O$_4$/NiO sheets can generate current densities of 10 and 20 mA/cm$^2$ upon application of 1.59 and 1.62 V potentials, respectively (Figure 4a,b). Current density successively increases with the increase in applied potential. NiCo$_2$O$_4$/NiO sheets are catalytically more active for OER compared to bare NiCo$_2$O$_4$ and NiO (Figure 4a). Bare NiCo$_2$O$_4$ requires 1.66 V to generate a current density of 10 mA/cm$^2$, whereas NiO requires 1.77 V. It is also clear from this result that the electrocatalytic activity of NiCo$_2$O$_4$ is better compared to that of NiO. The catalytic activity of NiCo$_2$O$_4$/NiO sheets is also compared to the physical mixture of NiO and NiCo$_2$O$_4$ having the same composition ratio. It is observed that the physical mixture sample shows higher electrocatalytic activity compared to bare NiCo$_2$O$_4$ and bare NiO. NiCo$_2$O$_4$/NiO pm required 1.60 V to generate a current density of 10 mA/cm$^2$ (Figure S10). The electrocatalytic efficiency of NiCo$_2$O$_4$/NiO sheets was compared to that of RuO$_2$. In the present reaction condition, RuO$_2$ can generate current densities of 10 and 20 mA/cm$^2$ upon application of 1.58 and 1.64 V versus RHE (Figure 4a,b), respectively, which also shows that the electrocatalytic activities of the NiCo$_2$O$_4$/NiO sheets are comparable to RuO$_2$. Nonfaradic capacitive current allied with...
NiO (101 mV/decade). This also signifies the presence of NiCo2O4. At potential 1.65 V versus RHE, mass activities of NiCo2O4/NiO sheets, values of Tafel slope were determined from the electrochemical double-layer charging current is calculated first, and from that, electrochemically active surface area (ECSA) of NiCo2O4/NiO sheets and NiCo2O4 is determined. Figure S11a,b shows the cyclic voltammetry (CV) curve recorded in the potential of 1.025–1.225 V versus RHE applying different scan rates in 1 M NaOH. From the CV curves, double-layer charging current is measured at a potential of 1.125 V versus RHE and plotted against scan rate. A straight line is observed, from the slope of which, Cdl (double-layer capacitance) can be calculated, and the values are 0.479 and 0.200 mF for NiCo2O4/NiO sheets and NiCo2O4, respectively (Figure S11c). The ECSA are calculated to be 7.89 and 3.34 cm², and the roughness factors are 112 and 47, respectively. Higher ECSA and roughness factor further strengthen the fact that the interconnected sheet like structure of NiCo2O4/NiO has increased surface area and that a certain percentage of NiO plays an important role to enhance the electrocatalytic activity of NiCo2O4. At potential 1.65 V versus RHE, mass activities of NiCo2O4/NiO, NiO, and NiCo2O4 were calculated to be 29.31, 8.05, and 1.40 A/g, respectively. Mass activity of NiCo2O4/NiO is higher compared to others, which reflects its higher catalytic activity. Specific activity (from ECSA surface area)²¹,²² was also calculated for both NiCo2O4/NiO and NiCo2O4, and the values are shown in Table 1. Higher mass and specific activities of NiCo2O4/NiO sheets reflect the higher catalytic activity. Intrinsic catalytic activity of the synthesized catalysts was further evaluated from turnover frequency (TOF), accepting that all of the metal atoms present on the electrode surface are catalytically active. TOF was calculated for NiCo2O4/NiO, bare NiCo2O4, and bare NiO at a fixed potential of 1.65 V versus RHE. Calculated TOF values are shown in Table 1. It is observed that NiCo2O4/NiO catalyst exhibits the highest TOF of ~1.4 × 10⁻⁴ s⁻¹ at a potential of 1.65 V versus RHE, which is 2.8 times higher than bare NiCo2O4 and 70 times higher than bare NiO. This result suggests that NiCo2O4/NiO can serve as an efficient and stable catalyst for water oxidation.

To judge the superior electrocatalytic activity of NiCo2O4/NiO sheets, values of Tafel slope were determined from the polarization curve. Figure 4d evidently shows that NiCo2O4/NiO has a Tafel slope value of 61 mV/decade, which is lower compared to bare NiCo2O4 (139 mV/decade, Figure 4d) and NiO (101 mV/decade). This also signifies that NiO present in NiCo2O4 helps to enhance the electrocatalytic activity of NiCo2O4. NiCo2O4/NiO-3 h is more active compared to NiCo2O4/NiO-15 h (Figure S12). The remarkably enhanced electrocatalytic activity may be attributed to the interconnected sheet like structure, which is helpful for ready charge transportation and also offers electrolyte to penetrate inside and easily contact with the active centers of the catalyst. NiCo2O4 has the spinel structure with more active sites, and NiO offers higher conductivity to NiCo2O4. Long-term durability of the NiCo2O4/NiO sheets was checked up to 500 cycles for OER. Result show that there is 100% current retention (Figure S13), which proves that the as-synthesized NiCo2O4/NiO was determined at a fixed potential of 1.64 V versus RHE up to 11 h, and the plots are shown in Figure S15. From Figure S15, it is very clear that the NiCo2O4/NiO can show unaltered current density up to 11 h under experimental condition. To gain insight into the superb performance for providing unaltered current density for longer period, PXRD and SEM analyses were carried out after electrocatalysis. From the PXRD pattern, it is clear that the electrode material remains in the same phase as before, and is shown in Figure S14. Figure S15 shows the SEM analysis data of the electrode material, which confirm that the morphologies of NiCo2O4/NiO are all well maintained. We have made a detailed comparison, where NiCo2O4 was used as OER catalyst, and the results are shown in Table S1. Electrocatalytic activity of NiCo2O4/NiO is comparable to the existing literature.

Electrochemical impedance spectroscopy (EIS) analysis was carried out to know the feasibility of the charge transportation on the electrode surface. Semicircle observed in the Nyquist plots can be fitted with an equivalent circuit, which is composed of Rs (solution resistance), constant-phase element, and Rct (charge-transfer resistance). Values of Rs and Rct are dependent on the electrocatalytic activity of the material, and lower the value faster is the reaction kinetics. Impedance result is shown in Figure 4c and the inset of Figure 4c. In case of NiCo2O4/NiO sheets, it is observed that Rs = 12.09 Ω and Rct = 29.36 Ω. The Rs values of NiCo2O4 and NiO are 15.88 and 16.77 Ω, respectively, which reflect that the solution resistance is higher for both the samples compared to NiCo2O4/NiO sheets. The Rct values of NiCo2O4 and NiO are 100 and 667 Ω, respectively, which are higher compared to NiCo2O4/NiO sheets. Lower charge-transfer resistance means higher conductivity, which is in accordance with the electrocatalysis data. To compare the electrocatalytic activity, EIS analysis of

Table 1. Comparative Result for Overall OER Activity for Different Catalysts

| anode      | potential (V) required to generate 10 mA/cm² | mass activity (A/g) at 1.65 V vs RHE | Tafel slope (mV/decade) | specific activity (mA/cm² ECSA) | TOF at 1.65 V vs RHE (s⁻¹) |
|------------|---------------------------------------------|-------------------------------------|-------------------------|---------------------------------|-----------------------------|
| NiCo2O4/NiO| 1.59                                        | 29.31                               | 61                      | 0.273                           | 0.014                        |
| NiCo2O4    | 1.66                                        | 8.05                                | 139                     | 0.179                           | 0.005                        |
| NiO        | 1.77                                        | 1.40                                | 101                     | 0.273                           | 0.0002                       |

Figure 5. i–t data recorded on NiCo2O4/NiO at a fixed potential of 1.64 V vs RHE in 1 M NaOH solvent.
NiCo$_2$O$_4$–NiO pm is also carried out, which shows that the solution resistance is 18.39 and the charge-transfer resistance is 50.7 Ω (Figure S10). All the $R_s$ and $R_{CT}$ values are shown in Table 2. This result also suggests that in the presence of little amount of NiO in NiCo$_2$O$_4$, even though in physical mixture, conductivity increases. A low $R_{CT}$ of NiCo$_2$O$_4$/NiO sheets suggests that NiCo$_2$O$_4$/NiO is electrocatalytically very active.

### 3. CONCLUSIONS

In summary, we have demonstrated a way to synthesize NiCo$_2$O$_4$ interconnected sheet like structure with ∼13% NiO. This novel 2D interconnected sheet like structure exhibits excellent electrocatalytic activity toward OER reaction. On the basis of our literature survey, there is no report for the electrocatalytic activity toward OER compared to bare NiCo$_2$O$_4$ and NiO. NiCo$_2$O$_4$–NiO pm shows excellent stability under OER condition.

### 4. EXPERIMENTAL SECTION, MATERIALS, INSTRUMENTATION, AND METHODS

#### 4.1. Synthesis of NiCo$_2$O$_4$/NiO Sheets

Following a simple wet-chemical route, NiCo$_2$O$_4$/NiO was synthesized. Co(NO$_3$)$_2$·6H$_2$O (1.5 mmol) was dissolved in 10 mL of water and, on the other hand, Co(NO$_3$)$_2$·6H$_2$O (3 mmol) was dissolved in 10 mL of water and mixed thoroughly. Then, urea (54 mmol) was added with 40 mL of poly(ethylene glycol). Then, hydrothermal reaction was carried out at 110 °C for 6 h. Finally, the product was collected, washed with deionized water and ethanol, and dried at 60 °C. Then, it was calcined at 300 °C for 3 h and the final product was collected for further characterization and application.

#### 4.2. Synthesis of NiCo$_2$O$_4$ via Hydrothermal Technique

Ni(NO$_3$)$_2$·6H$_2$O (1.5 mmol) was dissolved in 10 mL of water and, on the other hand, Co(NO$_3$)$_2$·6H$_2$O (3 mmol) was dissolved in 10 mL of water and mixed thoroughly. Then, urea (54 mmol) was added with 40 mL of poly(ethylene glycol). Then, hydrothermal reaction was carried out at 110 °C for 6 h. Finally, the product was collected, washed with deionized water and ethanol, and dried at 60 °C. Then, it was calcined at 300 °C for 3 h and the final product was collected for further characterization and application.

#### 4.3. Synthesis of NiO Sheets

Following a simple wet-chemical route, NiO was synthesized. Ni(II)-chloride hexahydrate was used as the precursor of nickel. Ni(II)-chloride hexahydrate (6 mL, 0.1 mol/L) was thoroughly mixed with 5 g of glucose and 1 g of urea. This mixture was stirred and heated at 140 °C for 6 h in air. After that, the black flocculated product was collected and calcined at 500 °C for 10 h in air.

#### 4.4. Electrochemical Measurement

Electrochemical measurements were carried out in a three-electrode system. For oxygen evolution reaction, 10 mL of 1 M NaOH was used as electrolyte. In the cell, Ag/AgCl was used as reference electrode, Pt wire as the counter electrode, and sample deposited on glassy carbon electrode was used as the working electrode. All of the electrochemical data were recorded in CHI604E (CH Instruments) at 25 °C. For oxygen evolution reaction, the potential range was 0–0.8 V versus Ag/AgCl at a scan rate of 2 mV/s.

#### 4.5. Preparation of Working Electrode

Ink of NiCo$_2$O$_4$/NiO and NiCo$_2$O$_4$ pm, NiCo$_2$O$_4$–NiO pm, and RuO$_2$ was prepared by dispersing 5 mg of the sample in 300 μL of 2-propanol. Then, 30 μL of Nafion was added as binder and sonicated for 30 min to have a uniform dispersion. After that, 5 μL of the dispersion was drop-casted carefully on GC electrode having a diameter of 3 mm, which leads to a catalyst loading of 1.06 mg/cm$^2$.

#### 4.6. Electrochemical Impedance Spectroscopy

Electrochemical impedance measurement was also performed in a three-electrode system. Onset potentials of different materials were chosen as the performing bias for this measurement with the sweeping of frequency of 50 kHz to 1 Hz with a 10 mV alternating current dither.

#### 4.7. Characterization of Materials

A Rigaku MiniFlex II diffractometer with Cu Kα radiation was utilized to monitor the powder X-ray diffraction pattern at a scanning rate of 2°/min. Raman analysis was carried out using an Airix (STR 500) instrument. The morphology of the NiCo$_2$O$_4$/NiO, NiCo$_2$O$_4$ sample was investigated using a Nova NanoSEM 450 field emission scanning electron microscope. Bruker XFlash 6130, attached with an FESEM instrument, was used for EDS analysis. The morphology of the NiCo$_2$O$_4$/NiO, NiCo$_2$O$_4$ sample was determined using transmission electron microscopy (operated with a Bruker microscope). X-ray photoelectron spectroscopy (XPS) analysis was carried out using a commercial Omicron EA 125 source with Al Kα radiation (1486.7 eV). For all measurements, the emission current of the X-ray source was fixed at 20 mA for an anode voltage of 15 kV. High-resolution XPS images were collected using a pass energy of 20 eV with a step size of 0.02 eV. The ultrahigh vacuum chamber base pressure was maintained at <10$^{-9}$ mbar throughout the measurements. To compensate for any kind of charging effect, the C 1s binding energy peak at 284.5 eV has been used as a reference.

#### 5. CALCULATION METHOD

Details of the calculations of mass activity and specific activity are given below. The mass activity (A/g) was calculated from the catalyst loading and the observed current density (mA/cm$^2$) at a potential of 1.65 V versus RHE.

$$\text{mass activity} = \frac{\text{observed current density}}{\text{fixed potential/catalyst loading}}$$

The specific activity is calculated by normalizing the current at a fixed potential (1.65 V vs RHE) by the electrochemically active surface area.

$$\text{specific activity} = \frac{\text{observed current}}{\text{electrochemically active surface area}}$$
TOF value was calculated for NiCo$_2$O$_4$/NiO, NiCo$_2$O$_4$, and NiO assuming that every metal atom is taking part in the catalysis reaction.

$$\text{TOF} = \frac{\text{observed current density at a fixed potential 1.65 V vs RHE} \times \text{geometric surface area}}{4 \times F \times n}$$

where 4 means four electrons are required to generate 1 mol of O$_2$ from H$_2$O, F is the Faraday constant (96 485.3 C/mol), and n is the moles of metal atoms present on the electrode surface. The value of n is calculated from the molecular weight of the compound and the amount of catalyst present on the electrode surface.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00957.

Experimental section, material characterization, calculation method, additional characterization, and electrocatalysis data (PDF)

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Notes

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