Fast microwave-assisted preparation of nickel–copper–chromium-layered double hydroxide as an excellent electrocatalyst for water oxidation†

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Herein, we describe a simple microwave method for the doping of Cu²⁺ into NiCr-LDH and the preparation of ternary Ni₂.25Cu₀.75Cr-LDH as a superior electrocatalyst for water oxidation in a neutral solution. The obtained Ni₂.25Cu₀.75Cr-LDH was characterized by XRD, DRS, TEM and FE-SEM techniques. The results showed that Ni₂.25Cu₀.75Cr-LDH was formed with a size of 30 nm. In order to examine the water oxidation activity of Ni₂.25Cu₀.75Cr-LDH, the as-prepared samples were used as an electrocatalyst-modified carbon paste electrode in neutral solution. The electrochemical results revealed that the optimized Ni₂.25Cu₀.75Cr-LDH presented extraordinary water oxidation activity with a low onset potential of 1.40 V (vs. RHE) and an overpotential of 170 mV compared to other molar ratios (Ni₂.5Cu₀.5Cr-LDH), (Ni₂CuCr-LDH), and bimetallic (CuCr-LDH), and even outperformed NiCr-LDH. Also, a small Tafel slope of 31 mV and high durability of 14 h could be obtained for Ni₂.25Cu₀.75Cr-LDH. The excellent OER could be assigned to the decreased band gap energy and increased charge transfer at Ni₂.25Cu₀.75Cr-LDH. Therefore, Ni₂.25Cu₀.75Cr-LDH is a promising water oxidation catalyst owing to its improved charge transfer ability.

1. Introduction

The application of renewable energy is a way to reduce dependence on fossil fuels. The rapid expansion of alternative energy technologies has recently triggered research on improved oxygen evolution reaction (OER) as an energy carrier. OER refers to the reaction of O₂ production during electrochemical water oxidation and is regarded as significant for storage application and energy conversions. The electrolysis of H₂O for oxygen evolution involves multi-step proton-coupled electron transfer with slow kinetics, with the OER requiring voltages greater than 1.23 V. Finding effective and low cost electro-catalysts for water oxidation is an important problem, which can carry out the reaction quickly and reduce the onset potential, thereby improving the efficiency of the reaction. Electro catalysts such as iridium and ruthenium oxides are active for oxygen evolution, but their scarcity and high cost limit their usage in water oxidation. Numerous studies have been reported on improving transition metal electrocatalysts. However, the catalytic activity of such materials is lower than that of iridium and ruthenium oxides. Thus, improving the efficiency of electrocatalysts is still a massive challenge.

Layered double hydroxides (LDHs) are a family of hydrotalcite-like materials. LDHs are scarce in nature though they can be easily prepared. The general formula is [M₁–xM’x⁺(OH)₂]ₓ⁰(An⁻)ₓ/n·mH₂O. In this structure, the positive charge is made by replacing the divalent metals with trivalent metals, with the positive charges neutralized by anions. LDHs have been applied in areas such as catalysis, ion exchange materials, energy exploitation, and electrocatalysis. Among LDHs, Ni-based materials, such as NiFe-LDH, NiCo-LDH, and NiV-LDH, have been studied as promising electrocatalysts for highly active water oxidation. However, few studies have been done on NiCr-LDH and NiCu-LDH for water oxidation due to the low catalytic activity of Cr and Cu ions as well as the weak synergistic effects between Ni and Cr or Cu. Moreover, the hydroxides of Ni act as insulators. Thus, the design of Ni-based hydroxides with good electronic conductivity is required. However, Cr(III)-based materials have improved conductivity, but they have no desirable OER activity because Cr³⁺ has the electron configuration of t⁸g5e⁶, which is desirable for improved conductivity. Thus, doping copper...
ions into the structure of nickel-chromium LDHs can be an excellent proposal to amend the conductivity of Ni hydroxide. Also, incorporating a third metal can correct the activity of electrocatalysts.

Here, we prepared tri-metallic Ni$_{2.25}$Cu$_{0.75}$Cr-LDH via the simple microwave method as an active and stable water oxidation electrocatalyst in neutral media. Our study deals with (i) multivalent cations of Ni, Cu and Cr that supply opportunities for interactions with metal hydroxide within generated electrons and increase the synergy between Ni and Cr towards water oxidation, thus enhancing the catalytic activity; (ii) the doping of an optimal amount of Cu ions into NiCr-LDH can decrease the bandgap energy and improve the charge transfer that has a positive effect on the OER reaction; (iii) the electrocatalyst prepared within a short time is an essential and significant need for large-scale water oxidation. The electrochemical data showed that the tri-metallic NiCuCr-LDH with the atomic ratio of Ni : Cu : Cr = 2.25 : 0.75 : 1 exhibited the best oxygen evolution activity compared to NiCr-LDH, NiCr LDH, and other NiCuCr-LDHs. Also, the stability of the tri-metallic Ni$_{2.25}$Cu$_{0.75}$Cr-LDH was confirmed by the chronoamperometry technique. These data introduce an earth-abundant electrocatalyst with high activity for water oxidation.

2. Experimental

2.1. Materials
Nickel(II) nitrate hexahydrate (Ni(NO$_3$)$_2$·6H$_2$O, Merck), chromium(III) nitrate nonahydrate (Cr(NO$_3$)$_3$·9H$_2$O, Merck), copper(n) nitrate hexahydrate (Cu(NO$_3$)$_2$·6H$_2$O, Merck), sodium carbonate (Na$_2$CO$_3$) and sodium hydroxide (NaOH, Sigma Aldrich) were applied without any purification.

2.2. Characterization
Field emission scanning electron microscopy (FE-SEM) graphs were recorded using a TESCAN model Mira 3-XMU instrument equipped with the elemental mapping analysis. Transmission electron microscopy (TEM) images were recorded using a TEM device model H9500. X-ray diffraction (XRD) patterns were obtained on a Bruker AXS X-ray diffractometer with Cu Kα radiation (voltage = 40 kV, current = 35 mA and wavelength = 0.154178 nm). Fourier-transform infrared spectroscopy (FT-IR) curves were recorded on a Shimadzu FT-IR model Prestige 21 spectrometer using a potassium bromide tablet. Atomic emission spectroscopy was used for the metallic elemental analysis. The atomic emission spectroscopy was performed in a 0.1 M sodium phosphate buffer solution (pH = 7). The electrochemical impedance spectroscopy (EIS) was performed in a frequency range of $10^6$ Hz–0.1 Hz at 1.92 V (vs. RHE). In addition, the chronocoulometry was exploited to investigate the stability of the samples in sodium phosphate buffer (0.1 M) at a potential of 1.78 V (vs. RHE) for 14 h. Also, in this research, all the potential data were converted into the RHE potential by the following equations:

\[ E_{\text{RHE}} = E_{\text{SCE}} + 0.242 + 0.059 \text{ pH} \]  
\[ \eta (V) = E_{\text{RHE}} - 1.23 (V) \]

3. Results and discussion

3.1. Physical characterization

3.1.1. X-ray diffraction. Fig. 1 presents the XRD patterns of the as-prepared NiCr-LDH and Ni$_{2.25}$Cu$_{0.75}$Cr-LDH. The crystalline phase and peak patterns of these materials were similar to materials that have been reported as layered materials. In all two cases, the patterns showed a series of peaks labeled as (003), (006), (101), (012), (015), (018), (110) and (113), which confirm the synthesis of layered double hydroxide materials. The (003) lattice plane appeared at a low angle and is a func-
tion of the basal spacing. In this study, the basal spacing for NiCr-LDH and Ni\textsubscript{2.25}Cu\textsubscript{0.75}Cr-LDH was about 0.76 and 0.75 nm, indicating the intercalation of the carbonate anion in the interlayer space.\textsuperscript{28} The patterns confirm that Ni\textsubscript{2.25}Cu\textsubscript{0.75}Cr-LDH and NiCr-LDH have a well-crystallized phase, and after the replacement of Cu\textsuperscript{2+} instead of Ni\textsuperscript{2+}, no change is observed at the layered structure of LDHs. It is known that parameter “a” corresponds to the average distance of the metal ions in the layer and shows the density of the metal ions on the crystal plane (003).

\[ a = 2d_{110} \]

It can be concluded that the replacement of copper with nickel in Ni\textsubscript{2.25}Cu\textsubscript{0.75}Cr-LDH, in comparison with NiCr-LDH, causes a slight increase in the “a” lattice parameter from 0.30 to 0.31 nm, suggesting that the ionic radius for Cu\textsuperscript{2+} is larger compared to Ni\textsuperscript{2+}. The ionic radii for Cu\textsuperscript{2+} and Ni\textsuperscript{2+} were 73 and 70 pm, respectively. Besides, the parameter “c” indicates the three times distance between the layers.\textsuperscript{29} The “c” parameter (\( = 3d_{003} \)) decreases from 2.28 to 2.20 nm with the increase in the size of the trivalent metal cations due to the degree of hydration of Ni\textsubscript{2.25}Cu\textsubscript{0.75}Cr-LDH compared to NiCr-LDH. Also, decrease in the “c” parameter of Ni\textsubscript{2.25}Cu\textsubscript{0.75}Cr-LDH can be explained by the Jahn–Teller effect. Cu\textsuperscript{2+} (d\textsuperscript{9}) ion showed a strong Jahn–Teller effect with an elongated axial M–O distance that led to poor long-range ordering.\textsuperscript{30,31} The shift of diffraction to higher angles in Ni\textsubscript{2.25}Cu\textsubscript{0.75}Cr-LDH (2\( \theta = 11.99^\circ \)) compared to those in NiCr-LDH (2\( \theta = 11.63^\circ \)) may be due to the distortion of the copper sites.

3.1.2. FE-SEM and TEM images. Fig. 2(a) and Fig. S1† present the morphology of Ni\textsubscript{2.25}Cu\textsubscript{0.75}Cr-LDH investigated by TEM and FE-SEM graphs. From Fig. 2(a) and Fig. S1, it is confirmed that Ni\textsubscript{2.25}Cu\textsubscript{0.75}Cr-LDH had a plate-like morphology as expected. The average thickness of the nano-plate was found to be 30 nm, and the hetero-structure of Ni\textsubscript{2.25}Cu\textsubscript{0.75}Cr-LDH was formed. The corresponding elemental mapping of Ni\textsubscript{2.25}Cu\textsubscript{0.75}Cr-LDH was analyzed to study the composition of elements in the as-prepared product, consisting of Ni, O, Cu, and Cr without any other impurity [see Fig. 2(b(b1, b2, b3 and b4))]. Also, as shown in Fig. 2[b(b1, b2, b3 and b4)], a unique distribution of Ni, Cu, and Cr is observed at Ni\textsubscript{2.25}Cu\textsubscript{0.75}Cr-LDH, providing efficient generation of electrons causing the good water oxidation activity. Besides, according to inductively coupled plasma (ICP) results (Table S1†), the obtained data from the ICP method for Ni, Cr and Cu agree with the starting ratio of metal salts.

3.2. Water oxidation

The water oxidation activity of tri-metallic Ni\textsubscript{2.25}Cu\textsubscript{0.75}Cr-LDH was measured by linear sweep voltammetry (LSV) in 0.1 M sodium phosphate buffer as the medium (pH = 7). As expected, CuCr-LDH and NiCr-LDH displayed poor water oxidation efficiency due to few active sites and unsuitable electrical conductivity. As shown in Fig. 3, the overpotential for starting water oxidation at CuCr-LDH and NiCr-LDH were 475 and 395 mV, respectively. The loading of Cu\textsuperscript{2+} into NiCr-LDH improved the oxygen evolution reaction (OER). Ni\textsubscript{2}CuCr-LDH needs an overpotential of about 325 mV for starting water oxidation, which was higher than that of Ni\textsubscript{2.5}Cu\textsubscript{0.5}Cr-LDH (255 mV). It is appealing to note that the water oxidation activity of tri-metallic NiCuCr-LDHs can be further improved.
by loading 0.75 mol Cu$^{2+}$ into NiCr-LDH. As a result, Ni$_{2.25}$Cu$_{0.75}$Cr-LDH can decrease the water oxidation overpotential from 395 to 175 mV. Based on the obtained test results, the optimal amount of loading of Cu$^{2+}$ into NiCr-LDH was about 0.75 mol, which was applied in all experiments. When the amount of Cu$^{2+}$ was higher than the optimal amount, the increasing resistance diminished the OER activity. As reported in Fig. 3(a), the overpotential for RuO$_2$ was about 225 mV, but the current density was smaller for Ni$_{2.5}$Cu$_{0.5}$Cr-LDH, confirming that Ni$_{2.25}$Cu$_{0.75}$Cr-LDH and Ni$_{2.5}$Cu$_{0.5}$Cr-LDH were better electrocatalysts compared to RuO$_2$.

Since sunlight agitates the water-splitting process at a current density of about 10 mA cm$^{-2}$, the required potential to achieve such current density is a significant factor. Ni$_{2.25}$Cu$_{0.75}$Cr-LDH only required 280 mV overpotential for achieving 10 mA cm$^{-2}$ current density, while NiCr-LDH needed 430 mV. Therefore, Ni$_{2.25}$Cu$_{0.75}$Cr-LDH showed better OER activity than NiCr-LDH. Also, the overpotential for achieving 10 mA cm$^{-2}$ current density in RuO$_2$ was about 395 mV. The comparative data for Ni$_{2.5}$Cu$_{0.5}$Cr-LDH, Ni$_{2.25}$Cu$_{0.75}$Cr-LDH, Ni$_2$CuCr-LDH, RuO$_2$, and NiCr-LDH at the current densities of 10 and 50 mA cm$^{-2}$ are presented in Fig. 4.

To compare the electrocatalytic activity of Ni$_{2.25}$Cu$_{0.75}$Cr-LDH towards water oxidation, a comparative study from the as-prepared electrocatalyst and those reported in the literature was conducted, as summarized in Table S2.$^\dagger$ To deeply study the effects of doping Cu$^{2+}$ in NiCr-LDH, diffuse reflectance spectroscopy (DRS) of NiCr-LDH and Ni$_{2.25}$Cu$_{0.75}$Cr-LDH was carried out (Fig. S2). Based on DRS and Tauc plot, the bandgap energy for NiCr-LDH was calculated to be about 2.2 eV, while for Ni$_{2.25}$Cu$_{0.75}$Cr-LDH, narrow bandgap energy of about 1.7 eV was observed. Therefore, doping an optimal amount of Cu$^{2+}$ into NiCr-LDH decreased the bandgap energy and improved the conductive electronic structure.$^{34}$ Also, the increased OER activity of Ni$_{2.25}$Cu$_{0.75}$Cr-LDH can be illustrated using the low Tafel slope. As revealed in Fig. 5, the Tafel slope of Ni$_{2.25}$Cu$_{0.75}$Cr-LDH was 31 mV dec$^{-1}$, which was lower than the slope for NiCr-LDH (34 mV dec$^{-1}$) and CuCr-LDH (40 mV dec$^{-1}$). So, loading copper into NiCr-LDH can enhance the water oxidation due to the facile electron transfer on the surface of Ni$_{2.25}$Cu$_{0.75}$Cr-LDH.$^{35}$ Recently, Ye et al. found that NiCr-LDH, Ni, and Cr moiety are active sites for water oxidation.$^{21}$ Hence, the role of the copper cation in improving the water oxidation of Ni$_{2.25}$Cu$_{0.75}$Cr-LDH
can be attributed to the decrease in the bandgap energy and increase in the charge transfer kinetics.

The higher water oxidation activity of Ni$_{2.25}$Cu$_{0.75}$Cr-LDH may be correlated to the higher charge transfer compared to NiCr-LDH and CuCr-LDH. To investigate the charge transfer, electrochemical impedance spectroscopies (EIS) of Ni$_{2.25}$Cu$_{0.75}$Cr-LDH, NiCr-LDH and CuCr-LDH electrocatalysts were conducted in a three-electrode system. The Nyquist curves of the electrocatalysts presented a clear semicircle (Fig. 6) that may be due to charge transfer resistance ($R_{ct}$) between the as-prepared electrocatalyst and electrolyte.$^{6,37}$ The diameter of the semicircle in the Nyquist curve as a parameter was applied to study charge-transfer resistance, where the small diameter of the impedance arc (DIA) has lower charge-transfer resistance at water oxidation.$^{38,39}$ As shown in Fig. 6, the DIA of Ni$_{2.25}$Cu$_{0.75}$Cr-LDH was small in comparison to that of NiCr-LDH and CuCr-LDH. This indicates low charge transfer resistance at Ni$_{2.25}$Cu$_{0.75}$Cr-LDH, thus improving the conductivity of Ni$_{2.25}$Cu$_{0.75}$Cr-LDH, which is in agreement with high water oxidation.

Furthermore, the OER stability of Ni$_{2.25}$Cu$_{0.75}$Cr-LDH was studied in 0.1 M sodium phosphate buffer (pH = 7). Fig. S3(a)$^\dagger$ shows that in the chronoamperometric process Ni$_{2.25}$Cu$_{0.75}$Cr-LDH could achieve a current density of about 14 mA cm$^{-2}$ when using an overpotential of 525 mV. The current density could remain stable for 14 h water oxidation reaction. Also, after the 14 h chronoamperometric process, Ni$_{2.25}$Cu$_{0.75}$Cr-LDH revealed an onset potential similar to the origin LSV [Fig. S3(b)$^\dagger$]. These results confirm that Ni$_{2.25}$Cu$_{0.75}$Cr-LDH is a promising electrocatalyst for water oxidation.

4. Conclusions

Trimetallic Ni$_{2.25}$Cu$_{0.75}$Cr-LDH was prepared via a simple microwave method within a short time. Then, it was studied as a water oxidation electrocatalyst in the neutral solution and carbon paste-modified method. According to the OER results, the optimized NiCuCr-LDH (Ni$_{2.25}$Cu$_{0.75}$Cr-LDH) displayed superior water oxidation activity with a low overpotential of about 170 mV and an onset potential of 1.40 V (vs. RHE), which have higher activity than other tri-metallic NiCuCr-LDHs, bimetallic NiCr-LDH and CuCr-LDH due to improved charge transfer. Based on the chronoamperometric test and LSV curve, the water oxidation reaction of Ni$_{2.25}$Cu$_{0.75}$Cr-LDH has long-term stability. Such development of water oxidation electrocatalysts is attributed to the doping of the Cu$^{2+}$ cation and the appropriate electron structure of Ni$_{2.25}$Cu$_{0.75}$Cr-LDH. The main activity of Ni$_{2.25}$Cu$_{0.75}$Cr-LDH makes it an electrocatalyst in the large-scale water oxidation process.

Conflicts of interest

There are no conflicts to declare.

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References