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Co Intake Mediated Formation of Ultrathin Nanosheets of Transition Metal LDH — an Advanced Electrocatalyst for Oxygen Evolution Reaction

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By controlling the ratio of tri- and bi-valent ions, multi-transition metals based layered double hydroxide (LDH) ultrathin nanosheets are synthesized. They show advanced OER performance with low overpotentials (~0.2 V) and decreased Tafel slopes with increasing Co incorporation due to the modulated electronic structures of catalytic centers and the increased surface area and electronic conductivity.

Water splitting to form H₂ and O₂, which would enable large scale storage of intermediate energy from renewable sources, has aroused intense studies recently. However, the energy efficiency of water splitting is significantly lost due to the slow kinetics of oxygen revolution reaction (OER). Therefore, an effective and stable catalyst to reduce the large overpotential and accelerate the OER reaction is highly required. Noble metal oxides such as IrO₂ and RuO₂ exhibit the best OER activity,[1] but the elemental scarcity and high cost have greatly hindered their widespread applications. Therefore, exploring earth abundant element based catalysts without compromising the high catalytic performances for OER is still a great challenge.

Recently, first low transition metal oxides and hydroxides have been under intensive scrutiny as low cost catalysts for renewable energy applications.[3] It has been found that the OER active materials are layered hydroxides or oxyhydroxides composed of edge sharing octahedral MO₆ layers,[2h, 3] and their activity could be further improved after the exfoliation process.[3a, 4] Meanwhile, many studies found that mixed metal hydroxides/oxides exhibit higher catalytic performance than their monary counterparts,[2g, 4a, 5] possibly related to the changed electronic structure[2f, 6] or the enhanced electrical conductivity[6a] of the catalyst with the incorporation of “impurities”. However, the precise roles of the primary transition metals as well as the “impurities” in improving the OER activity of catalysts still have not been unravelled.

In this work, without any further exfoliation treatments, bi- (FeNi) and tri-mental (Fe, Ni and Co) LDH with controlled Co incorporations and atomic thickness were successfully obtained by a one step hydrothermal method (see Scheme S1), which showed advanced OER activity with overpotential as low as 0.21 V and Tafel slopes ranging from 55 mV/dec to 42 mV/dec that decreased with increasing Co content. Besides the increased specific surface area with the increased Co incorporation, it was revealed that the increased number of the active sites, improved electronic conductivity as well as enhanced activity of the catalytic sites brought by the minor “impurities” (Fe and Co) also contributed to the superior electrochemical catalytic performances of the FeNiCo LDH ultrathin nanosheets towards OER.

Figure 1. SEM (A, B) images, XRD pattern (C), TEM image (D), AFM height image (E) and corresponding height as a function of position curve (F) of FeNi LDH nanosheets. Inset images in D is the enlarged TEM image of standing nanosheets showing the thickness of LDH.

FeNi LDH, which was reported to be an OER active material,[3a, 4] was synthesized via a hydrothermal method (see SI for detail). By precisely tuning the ratios of Fe³⁺ to Ni²⁺ in the mother solution, the as-formed product changed from Ni(OH)₂ in microscale to FeNi LDH in nanoscale (Figure S1). After exploring a variety of parameters, Fe/Ni=1/10 was identified as the best ratio for forming the ideal product. The scanning electron microscopy (SEM, Figure 1A, B) and transmission electron microscopy (TEM, Figure 1D, S2A) images show that they are nanosheets. The energy dispersive X-ray spectroscopy (EDX) mapping (Figure S3) revealed that they are nanosheets. The energy dispersive X-ray spectroscopy (EDX) mapping (Figure S3) revealed the uniform distribution of Fe and Ni in the formed nanosheets with Fe/Ni ratios to be 1/10, consistent with the X-ray photoelectron spectra (XPS) result (Figure S4). From the standing LDH nanosheet, the thickness of FeNi₁₀ LDH was measured to be ~2 nm (Figure 1D inset), which was further confirmed by the atomic force microscopy (AFM) height imaging (Figure 1E, F).
FeNiCo LDHs with tuneable Co contents were synthesized by precisely controlling the amount of added cobalt salt in the mother solution. The SEM (Figure S5A, D) and TEM (Figure S5B, E) images of these LDHs revealed that they are in platelet structures akin to that of FeNi$_{10}$ LDH (Figure 1). EDX mapping (Figure S6) showed the uniform distribution Fe, Ni and Co in the nanosheets. XPS spectra showed the intensity of Co increased with the increase of Co addition in mother solution (Figure S7). Moreover, both the EDS and XPS results suggested that the Fe/Ni/Co ratios of synthesized LDHs were 1/9/1 and 1/8/2, respectively, which were in good agreement with the corresponding solution stoichiometries. The XRD of FeNiCo LDHs (Figure S8) showed that only (003) diffraction peak remains pronounced whereas the (006) and (009) peaks become ambiguous due most likely to the ultrathin structure of the LDHs (only about two layers). This is consistent to the report of Hu et al., who showed that the (00n) diffraction peaks disappear once the bulk LDH is exfoliated into single layers.[a] Moreover, the (003) diffraction peak is positively shifted with the Co incorporation (Figure S8B) from 11.28° for FeNi$_{10}$ LDH to 11.45° and 12.9° for FeNi$_9$Co LDH and FeNi$_8$Co$_2$ LDH, respectively, suggesting a decrease in d-spacing along the c axis from 0.78 nm to 0.77 nm and 0.68 nm due to the substitution of Ni$^{2+}$ with Co$^{2+}$. Indeed, the TEM images (insets in Figure S5B, E) and the AFM height images (Figure S5C, F) show that with the increase of Co content, the thickness of LDHs decreases, namely from ~2 nm for FeNi$_{10}$ LDH (Figure 1D-F) to 1.5–1.8 nm for FeNi$_9$Co LDH (Figure S5C), and to 1.2–1.5 nm for FeNi$_8$Co$_2$ LDH (Figure S5F). To our knowledge, this is the first time that such FeNiCo LDH ultrathin nanosheets with tuneable FeNiCo ratios and thicknesses smaller than 2 nm are prepared.

Transition metal based ultrathin nanosheets with single or few atomic layers, are expected to have high surface activity and rich electronic properties that may render intriguing applications in energy storage and conversion.[7] Herein, the as-synthesized ultrathin FeNi and FeNiCo LDH nanosheets were investigated as electrochemical catalyst towards OER in a typical three-electrode configuration in 1 M KOH. Firstly, the FeNiCo LDHs were deposited onto Ni foam for cyclic voltammetry (CV) (Figure S9) measurements. We observed redox peaks at around 1.38 V, which correspond to the reversible reactions of Ni(II)/Ni(III) or IV)[2][3] for all the LDH samples. Moreover, the current density spiked at around 1.44 V, signalling the onset of water splitting. Further, linear sweep voltammetry (LSV) tests were used to investigate the catalytic activities of the set of OER catalysts after 95% Ir-correction (Figure 2A). Consistent to the CV results, the current density of catalyzed OER spiked around 1.44 V. The overpotentials of these FeNi and FeNiCo LDHs catalyzed OER are close to each other, suggesting that they have similar catalytic centres. Moreover, the low overpotential of 0.21 V indicates that they are among the most active non-noble metal based electrochemical catalyst for OER.[4][5, 9] Further, the FeNiCo LDH ultrathin nanosheets were loaded on glass carbon as working electrode. The LSV curves of OER (Figure S10A) confirmed the low onset potential of ~0.21 V, in agreement with the results obtained on the Ni foam electrodes. However, the current density of OER on GC electrode was smaller than that on Ni foam electrode at the same applied voltage (Figure S10B), due plausibly to the three-dimensional structure of Ni foam with a larger surface area. Apart from the intrinsically high catalytic activity of the transition metals used, the ultrathin nanosheet structure might also be important to the advanced catalytic performance of LDHs. First, layered hydroxides or oxhydroxides composed of edge sharing octahedral MO$_6$ layers were reported to be OER active, as observed in a NiOOH material in situ transformed from NiO,[2b] and further revealed in both amorphous Co-phosphate and Ni-borate catalysts and crystalline metal oxides.[3] Second, the layered structure is relatively open, thus permits fast diffusion of reactants or products and rapid proton-coupled electron transfer and allows the catalytic active sites easily accessible,[9] giving rise to the high electrocatalytic activity toward OER.[8b, 10] Moreover, the atomic thickness endows FeNi and FeNiCo LDH ultrathin nanosheets with improved surface activity than their bulk materials that further increased their OER performances.

![Figure 2. Electrocatalytic OER performance of the FeNiCo LDH nanosheets.](image_url)

(A) Linear sweep voltammetry polarization curves. (B) Tafel plots. (C) Electrochemical impedance of FeNiCo LDH with different Fe/Ni/Co ratios at overpotential of 0.3 V. (D) LSV curves of bare Ni foam, FeNi$_9$Co$_2$ LDH before and after chronopotentiometry test for 11 hours. Catalyst loading was ~0.25 mg/cm$^2$.

The potentials required to achieve the current density of 10 mA/cm$^2$, which is the approximately current density for a 10% efficient solar-to-fuel conversion device,[5a, 11] decreased with the increase of the Co incorporation (1.472V, 1.462 V, and 1.45 V for FeNi$_{10}$, FeNi$_9$Co, and FeNi$_8$Co$_2$ LDH, respectively), indicating a higher catalytic performance of FeNiCo LDH nanosheets with higher Co contents. N$_2$ adsorption-desorption isotherms (Figure S11) show that the specific surface area of FeNi$_{10}$ LDH, FeNi$_9$Co LDH, and FeNi$_8$Co$_2$ LDH were 46.05 m$^2$/g, 54.18 m$^2$/g and 80.44 m$^2$/g, respectively, which increased with the increase of Co incorporation and might lead to more exposed catalytic active sites.

Tafel slope describes the influence of potential on the steady-state current density and is an important factor for evaluating OER kinetics. The estimated Tafel slopes of the as-synthesized LDHs are 55 mV/dec, 52 mV/dec, and 42 mV/dec for FeNi$_{10}$ LDH, FeNi$_9$Co LDH, and FeNi$_8$Co$_2$ LDH, respectively (Figure 2B), which decreased with the increase of Co doping. It is worth noting that the value of FeNi$_8$Co$_2$ LDH catalyzed OER is close to that of the well-established OER catalysts of IrO$_2$ (~49 mV/dec)[2b, 12] as well as exfoliated LDH nanosheets (45, 41,
and 40 mV/dec for CoCo, NiCo, and NiFe LDH nanosheets, respectively,\cite{6b, 15} indicating an efficient electrocatalytic activity of synthesized FeNiCo LDH ultrathin nanosheets.

It is known that the high conductivity of catalysts would facilitate the charge transport, minimize the potential drop, and thus lead to good catalytic activities. Early in 1987, Corrigan et al.\cite{6a} found that the OER activity of Ni(OH)\textsubscript{2} was enhanced with Fe doping and an increased conductivity was hypothesized to be the critical factor. Recently, by studying the conductivity of Ni\textsubscript{1-x}Fe\textsubscript{x}OOH as a function of Fe content, Boetche et al.\cite{5a} confirmed that electronic conductivity of Ni\textsubscript{1-x}Fe\textsubscript{x}OOH film increased with Fe addition. In this work, the conductivities of both FeNi and FeNiCo LDH nanosheets were measured by electrochemical impedance spectroscopy (EIS, Figure 2C). The semicircle diameter in the high frequency range of the Nyquist plot is associated with the charge transfer resistance, which benefits the efficient charge transport, is partly due to the decreased thickness of LDH nanosheets, on top of the synergistic effect stemming from the multiple transition metals present, as well as other intrinsic factors, e.g., the dopant role of the Co in a way similar to Fe as a dopant to improve the conductivity of titanium.\cite{14}

Next, assuming that all of the metal ions in the catalysts were involved in the electrochemical reaction, the OER turnover frequencies (TOFs) at the overpotential of 0.3 V were calculated. It should be pointed out that the as-calculated TOFs could be gross underestimations of the actual TOFs because not every metal atom is catalytically active. Nevertheless, even with these overly conservative estimations, the TOFs are still respectable: 0.53 s\textsuperscript{-1} for FeNi\textsubscript{1-x} LDHs, 0.55 s\textsuperscript{-1} for FeNiCo LDHs and 0.7 s\textsuperscript{-1} for FeNiCo\textsubscript{2} LDHs, all higher than previously reported values under comparable measurement conditions.\cite{2h, 4b, 5a, 8b}

As the most active OER catalyst, the FeNi\textsubscript{1-x}Co\textsubscript{x} LDH nanosheets were investigated for assessing their stability. It outperformed the reported earth abundant metal hydroxide OER catalysts\cite{6a, 3a} at high current densities, such as 5 mA/cm\textsuperscript{2}, 10 mA/cm\textsuperscript{2}, and 20 mA/cm\textsuperscript{2}, by low required potentials at 1.441 V, 1.454 V, and 1.469 V, respectively (Figure S12). The high current density is ascribed to the high activity of the catalyst, because the bare Ni foam exhibited little current density of 10 mA/cm\textsuperscript{2}.

Figure S13B shows an increased activity of the FeNi\textsubscript{1-x}Co\textsubscript{x} LDH catalyst with anion adsorbrates\cite{16} and thus influence the binding of oxygen intermediate species and thus the OER activity.\cite{18} Take FeNi\textsubscript{1-x}Co\textsubscript{x} LDH as a typical example, XPS analysis was conducted (Figure S14) to better understand the oxidation state of catalytic metal ions. In the O 1s region, the spectra of FeNi\textsubscript{1-x}Co\textsubscript{x} LDH could be deconvoluted to four oxygen peaks, which correspond to Fe-O (531.4 eV), Ni-O (531.7 eV), Co-O (532.7 eV), and Co\textsuperscript{3+} and chemi-sorbed water at or near the surface (533.9 eV).\cite{20a, 20b, 21} The Co 2p feature of FeNi\textsubscript{1-x}Co\textsubscript{x} LDH (Figure S14B) was best fitted with two shakeup satellites (yellow curves), and two spin-orbit doublets, characteristic of Co\textsuperscript{2+} (blue curve) and Co\textsuperscript{3+} (green curve).\cite{22} The electronic configurations of Co\textsuperscript{2+} and Co\textsuperscript{3+} were most likely t\textsubscript{2g}\textsuperscript{6}e\textsubscript{g}\textsuperscript{2} and t\textsubscript{2g}\textsuperscript{5}e\textsubscript{g}\textsuperscript{2}, respectively. In the Ni 2p region of FeNiCo\textsubscript{2} LDH (Figure S14C), the binding energy of Ni peaks were positively shifted, suggesting the strong interactions involving Ni and
abundant OER catalysts reported thus far.

catalytic activity of these LDHs outperform most of earth
low as 0.21 V and Tafel slopes down to 42 mV/dec. The high
activity of catalytic center arising from the modulated
sites, reduced charge transference resistance and improved
as synthesized FeNiCo LDH increased with the increase of
In conclusion, transition metal LDH ultrathin nanosheets
were successfully synthesized. The as-prepared LDHs showed advanced
electrocatalytic performances on OER with overpotentials as
details, SEM, TEM, EDX, BET, XRD, XPS and CP of catalysts. See
Electronic Supplementary Information (ESI) available: Experimental

Notes and references

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