A wafer-scale 1.4 nm ultrathin Ni(OH)2 nanosheet was synthesized by ionic layer epitaxy. This free-standing Ni(OH)2 nanosheet was directly used to catalyze the oxygen evolution reaction (OER). At a current density of 10 mA cm\(^{-2}\), the overpotential reached 295 mV (vs. RHE) in Fe-rich 1 M NaOH. This 1.4 nm Ni(OH)2 nanosheet showed a very high turnover frequency of 5.47 s\(^{-1}\) and a mass activity of more than 2 \(\times 10^{5} \) A g\(^{-1}\) at an overpotential of 300 mV. Such a high electrocatalytic mass activity of the Ni(OH)2 nanosheet was more than 2 orders of magnitude higher than those of typical OER catalysts. The capability of producing wafer-scale nanometer-thick nanosheets offers a promising strategy to improve the mass efficiency of electrochemical catalysts, which is particularly valuable for preserving rare and precious catalyst materials.

Electrochemical water splitting is a promising strategy for converting electrical energy into chemical fuel.\(^1,2\) In a water-splitting system, electrocatalysts are normally used to facilitate the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) on the cathode and anode, respectively.\(^3,4\) Many transition-metal compounds, such as borides, nitrides, oxides, hydroxides, phosphides, sulfides, and selenides have been explored as promising candidates for OER catalysts.\(^5\)–\(^11\) Among them, Ni-based oxides/hydroxides appeared to be one of the most competitive materials which give a low overpotential and high current density due to the active species of Ni\(^{II/III}\) for OER catalysts.\(^12\)–\(^22\) Very recently, two dimensional (2D) nanomaterials, owing to their abundant active sites, delocalized spin states and high electrical conductivity, showed great promise for further promoting the electrochemical catalytic activity.\(^23\)–\(^29\) For example, metallic nanosheets of 1T-MoS\(_2\) grown on graphite showed a dramatically enhanced HER catalytic behavior.\(^23\) 2D nanostructured WSe\(_2\) manifested much higher performance for electrocatalytic CO\(_2\) reduction compared to bulk transition metal dichalcogenides.\(^24\) Although significantly enhanced catalytic performance was demonstrated in comparison with their bulk form, these materials intrinsically are not the optimal catalytic material selection. The best solution is to create 2D nanostuctures from the catalytic material to raise the existing good catalytic performance to a new level. The record high catalytic performance from nanometer-thicker Co-Co\(_2\)O\(_4\) is a good example of this strategy.\(^25\) However, since these materials typically do not have a layered crystal structure, they could only be made with sizes usually smaller than 1 µm. This remains a great challenge for system-level development where wafer-scale uniform thickness distribution is required. To address this challenge, here we report the development of a 1.4 nm Ni(OH)\(_2\) nanosheet OER catalyst on the wafer scale by ionic layer epitaxy (ILE). The uniform nanometer thickness of the Ni(OH)\(_2\) nanosheet across the entire wafer surface offered orders of magnitude higher mass electrochemical activity compared to typical OER catalysts. This development marks a new cornerstone for the development of an efficient electrochemical catalyst.

The Ni(OH)\(_2\) nanosheet was synthesized using nickel nitrate hexahydrate and hexamethylenetetramine (HMT) as precursors, and templated with a monolayer of oleic acid surfactant at the water surface (see the ESI\(^\dagger\) for the synthesis details). Due to the very low precursor concentration, growth only occurred at the polarized interface where the Ni\(^{2+}\) ions were concentrated within the electrical double layer. The growth mechanism is detailed in previous publications.\(^30\)–\(^32\) In this work, the interaction between the oleic acid and precursors could be briefly described as follows. At 60 °C, HMT decomposed into HCHO and ammonium hydroxide, forming an alkaline environment. Under alkaline conditions, oleic acid will dissociate into negatively charged olate. The positively charged Ni\(^{2+}\) ions were concentrated under the monolayer of olate, forming a Stern layer of Ni\(^{2+}\) ions. Then, the Ni\(^{2+}\) ions in the Stern layer could reach supersaturation and crystallize into a layer of Ni(OH)\(_2\). The critical nucleation size of Ni(OH)\(_2\)
could be limited by the carboxylic groups bonding to Ni(OH)\textsubscript{2} crystals. Due to the complete coverage of the surfactant monolayer, the Ni(OH)\textsubscript{2} nanosheet could be grown as large as the entire solution surface in the reactor. In order to transfer the entire nanosheet, a 3-inch Si wafer was placed at the bottom of the solution prior to the growth (Fig. 1a). By slowly removing the nutrient solution after the growth, the nanosheet was completely transferred to the Si wafer surface (Fig. 1b). After drying, the Si wafer still exhibited a very clear and smooth surface without any observable additives or non-uniform optical diffractions (Fig. 1c), confirming the extremely high wafer-scale uniformity. Fig. 1d is a typical SEM image of an as-transferred nanosheet on a Si substrate. No visible contrast variation could be observed because the nanosheet was continuous and uniform in thickness. The same featureless images were obtained for the entire substrate, revealing the extreme uniformity of the nanosheet geometry and coverage (Fig. S1†). A few small cracks could be found as shown in Fig. 1e, which was used to confirm the existence of the nanosheet. The atomic force microscopy (AFM) topography image revealed that the nanosheet surface was extremely smooth and flat (Fig. 1f). Sporadic particles observed on the nanosheet surface may be the contaminants picked up from the reaction solution during the transfer process. Two line profiles along the crack area were extracted and are shown in Fig. 1g, which confirmed that the thickness of the nanosheet was 1.4 nm and uniform across the entire nanosheet.

X-ray photoelectron spectroscopy (XPS) was employed to probe the elemental information and bonding states of the nanosheet. The full XPS survey spectra clearly showed the Ni, O, C and Si peaks detected from the as-transferred nanosheet on a Si substrate (Fig. 2a). To further reveal the chemical state of the Ni atom, the Ni 2p XPS peak of the nanosheet was individually scanned and deconvoluted (Fig. 2b). The peak at 853.5 eV can be attributed to Ni\textsuperscript{2+} in Ni(OH)\textsubscript{2}, evidencing that the bulk component of this nanosheet was Ni(OH)\textsubscript{2}.

Transmission electron microscopy (TEM) was then used to characterize the crystal structure of the Ni(OH)\textsubscript{2} nanosheets. Fig. 2c shows an as-synthesized nanosheet on a holey carbon TEM grid. Due to the extreme flexibility, wrinkles or overlaps could often be observed on the suspended regions. The high-resolution TEM (HRTEM) image revealed the polycrystalline feature of the Ni(OH)\textsubscript{2} nanosheet, where the individual domain was found to be ~5 nm (Fig. 2d). From the image, the (101) d-spacing was found to be 0.235 nm. The corresponding selective area electron diffraction (SAED) pattern exhibited a semi-continuous ring pattern (inset of Fig. 2c), in which the diffraction rings can be indexed to the (100), (101), (102) and (110) atomic planes of trigonal β-Ni(OH)\textsubscript{2} (space groups P\textsuperscript{3}m\textsubscript{1}, a = 0.312 nm, c = 0.46 nm, α = 90°, β = 90°, and γ = 120°).

To study the catalytic behavior associated with the ultra-small thickness towards the OER, the Ni(OH)\textsubscript{2} nanosheet was transferred onto a FTO glass (Fig. S2†). As a comparison, the OER activities of thicker Ni(OH)\textsubscript{2} layers, commercial RuO\textsubscript{2} and bare FTO glass were evaluated using the same configuration. The thicker Ni(OH)\textsubscript{2} layers were prepared by either ILE or
electrodeposition (see the Experimental section in the ESI and Fig. S3 and S4†) and their thicknesses were found to be 7.0 nm and 230 nm for these methods. The commercial RuO$_2$ was deposited on FTO by the solvent evaporation method (see the detailed information in the ESI and Fig. S5†). Fig. 3a illustrates the current density–overpotential ($j$–$\eta$) curves of the 1.4 nm Ni(OH)$_2$ nanosheet measured in 1 M NaOH solution in comparison with the other two thicker Ni(OH)$_2$ films, commercial RuO$_2$ and bare FTO. All of the Ni(OH)$_2$ samples can produce a geometric current density of 10 mA cm$^{-2}$ at $\eta = \sim 330$ mV, which agreed well with other reported NiO$_x$ OER catalysts.$^{7,12,17}$ The $j$ values of Ni(OH)$_2$ samples were larger than that of commercial RuO$_2$, and far higher than that of bare FTO. Moreover, it can be observed that all Ni(OH)$_2$ samples displayed an oxidation peak at $\eta$ from 100 mV to 200 mV (the peaks from the 1.4 nm and 7.0 nm Ni(OH)$_2$ samples were enlarged and are shown in Fig. 3b). This oxidation feature is related to the oxidation of Ni(OH)$_2$ to NiOOH,$^{12,20}$ and is reflective of the amount of active Ni sites. The large difference of the peak areas suggested that Ni atoms inside the bulk film were also electrochemically active. Du’s study showed that high oxidation state Ni$^{III/IV}$ can serve as an active species for OER catalysts.$^{15}$

From the oxidation peak in our work, it can be seen that the thicker Ni(OH)$_2$ samples have more Ni$^{III/IV}$ sites. But their OER performance is similar to that of 1.4 nm Ni(OH)$_2$ samples. Therefore, this result indicates that not all high oxidation states of Ni sites can catalyze the OER. To estimate the exposure of active sites, the electrochemical active surface area (ECSA) and the roughness factor (RF) were calculated by CV measurements at different voltage rates (see calculations in the ESI, Fig. S6 and Table S3†). The ECSA values in this work are smaller than those from other studies reported due to the low ECSA and RF of FTO glass.$^{18}$ The ECSA values of the electrodes that covered 1.4 nm, 7.0 nm and 230 nm Ni(OH)$_2$ layers are 0.037 cm$^2$, 0.035 cm$^2$, and 0.027 cm$^2$, respectively, indicating that the number of active sites is similar in different thickness Ni(OH)$_2$. Moreover, it can be observed that the ECSA and RF values of commercial RuO$_2$ were much higher than those of the Ni(OH)$_2$ samples (Fig. S6 and Table S3†). However, RuO$_2$ showed much lower OER performance compared to Ni(OH)$_2$. This result could be attributed to the good conductivity, but poor intrinsic OER catalytic activity of RuO$_2$.

Electrochemical impedance spectroscopy (EIS) was used to characterize the surface kinetics of the Ni(OH)$_2$ films, commercial RuO$_2$ and bare FTO. The Nyquist plots are shown in Fig. 3c and Fig. S7a and b.† An $R_\alpha(R_\varepsilon,C)$ equivalent circuit was used to fit the EIS parameters (as shown in Fig. S7c†), where $R_\alpha$ is the series resistance that includes the internal resistance of the electrode, $R_\varepsilon$ is the charge transfer resistance, and $C$ is the capacitance. The data are summarized in Table S4.† All the Ni(OH)$_2$ samples showed a very close $R_\varepsilon$, suggesting that there was no visible variation of the charge transfer resistance across the solid/electrolyte interface in these Ni(OH)$_2$-FTO electrodes. And it can be seen that the $R_\varepsilon$ values of bare FTO (15 052 Ω) and RuO$_2$ (380 Ω) are far higher than that of Ni(OH)$_2$ (about 70 Ω), which is consistent with the electrocatalytic measurements. By extrapolating the linear region of $\eta$ versus log $j$ (Fig. 3d and Fig. S8†), the Tafel slope values of the 1.4 nm, 7.0 nm, and 230 nm Ni(OH)$_2$ films, commercial RuO$_2$, and bare FTO, were determined to be 41, 55, 80, 90, and 140 mV per decade, respectively. The significantly lower Tafel slope of 1.4 nm Ni(OH)$_2$ was an indication of the largely promoted interfacial kinetics as the film thickness was reduced to the nanometer scale. The ultra-thin thickness ensured that all the charge separation in the film would occur in the space charge region with only ~1 nanometer diffusion length.

The mass activity of an electrocatalyst is particularly meaningful in commercial applications. As shown in Fig. 3e, a remarkable mass activity of 4662 A g$^{-1}$ was obtained from the 1.4 nm Ni(OH)$_2$ nanosheet at $\eta = 300$ mV, approximately 3.6, 120 and 650 times higher than that of the 7.0 nm Ni(OH)$_2$ layers, 230 nm Ni(OH)$_2$ layers, and commercial RuO$_2$, respectively. The intrinsic activity also plays a crucial role in optimizing the overall OER activity, which could be estimated by the turnover frequency (TOF). The TOF values are defined as the number of O$_2$ molecules evolved per electrochemically accessible Ni (or Ru) site per second. The TOF values were calculated by:

$$\text{TOF} = \frac{j \times A}{4 \times F \times m}$$

![Fig. 3](link)
where $A$ is the surface area of the electrode, $F$ is the Faraday constant, and $m$ is the number of moles of the catalyst. The $m$ of Ni(OH)$_2$ could be calculated from the effective thickness (ESI, Table S1†) and molecular weight of Ni(OH)$_2$. As shown in Fig. 3f, when a $\eta$ of 300 mV is applied, a TOF of 1.12 s$^{-1}$ is recorded for the 1.4 nm Ni(OH)$_2$ catalyst, that is about 3.6-, 120- and 450-times higher than that of the 7.0 nm and 230 nm Ni(OH)$_2$ layers and commercial RuO$_2$, respectively, further confirming the outstanding intrinsic activity of the ultrathin Ni(OH)$_2$ in OER catalysis. The significant enhancement in the electrocatalytic activity could be attributed to the largely facilitated electron transfer from the ultra-thin nanosheet to the substrate.

Moreover, the very recent work showed that an Fe-rich electrolyte could largely improve the OER activity of NiO, which depends on the role of Fe in the local structure, rather than in the bulk or on the average electrochemical properties of NiO. Herein, we measured the $j$–$\eta$ curve and Tafel slope in the Fe-rich NaOH electrolyte, and observed obviously enhanced catalytic activity (Fig. S9†). The mass activity and TOF values of 1.4 nm Ni(OH)$_2$ in the rich-Fe NaOH electrolyte further reached up to $2.0 \times 10^{4}$ A g$^{-1}$ and 5.47 s$^{-1}$ at $\eta = 300$ mV.

To evaluate the OER performance of the 1.4 nm Ni(OH)$_2$ nanosheet, the measured data were compared to other reported OER catalysts. The values of $\eta$, mass activity and TOF are summarized in Table 1. It can be clearly seen that the 1.4 nm Ni(OH)$_2$ nanosheet exhibited similar or slightly higher values in terms of $\eta$ as compared to typical electrocatalysts, including NiO, IrO$_2$, Ni–Fe oxide/LDH, and Co-based OER catalysts. And the overpotential we reported is still lower than that of other OER electrocatalysts reported recently (as shown in Table S5†). In particular, the TOF and mass activity of the Ni(OH)$_2$ nanosheet were significantly higher than other reported values. The mass activity and TOF reported by our group for Fe-rich electrolyte (Fig. 4a, red curve) compared with the initial one (Fig. 4a, black curve). Comparing the SEM images of the Ni(OH)$_2$ nanosheets before and after the long-term operation (Fig. S10e), no holes or any other types of damage could be found. The nanosheet exhibited excellent integrity even around the cracked areas (Fig. S10e) where the numbers of defects and active sites are usually high. Such a good electrochemical stability could be attributed to the overall short out-plane charge diffusion length enabled by the ultrathin 2D structure with uniform thickness. This could drastically improve the charge distribution uniformity and avoid the formation of hot

![Fig. 4](image)

Another important criterion for an OER catalyst is its operational stability. The stability of the 1.4 nm Ni(OH)$_2$ nanosheet was assessed in 1 M NaOH by recording the current density as a function of time at $\eta = 335$ mV. As shown in Fig. 4a, the $j$–$\eta$ curve of the 1.4 nm Ni(OH)$_2$ nanosheet exhibited no tendency of reduction after 15 hours of continuous oxygen evolution reaction. The $j$–$\eta$ curve also showed a very small declination (Fig. 4b, red curve) compared with the initial one (Fig. 4b, black curve). Comparing the SEM images of the Ni(OH)$_2$ nanosheets before and after the long-term operation (Fig. 4c and d), no holes or any other types of damage could be found. The nanosheet exhibited excellent integrity even around the cracked areas (Fig. S10f) where the numbers of defects and active sites are usually high. Such a good electrochemical stability could be attributed to the overall short out-plane charge diffusion length enabled by the ultrathin 2D structure with uniform thickness. This could drastically improve the charge distribution uniformity and avoid the formation of hot

### Table 1. OER performance comparison between this work and others

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\eta$ (mV)</th>
<th>Mass activity (A g$^{-1}$)</th>
<th>TOF (s$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(OH)$_2$ nanosheet</td>
<td>324 ± 4 (294$^*$)</td>
<td>5058 ± 562 (23322$^{2\circ}$)</td>
<td>1.22 ± 0.13 (5.47$^*$)</td>
<td>This work</td>
</tr>
<tr>
<td>2-3 nm NiO layer</td>
<td>334 ± 6</td>
<td>951 ± 106</td>
<td>0.24 ± 0.04</td>
<td>7</td>
</tr>
<tr>
<td>NiO nanoparticle</td>
<td>335 ± 5</td>
<td>40.7 ± 8</td>
<td>0.001 ± 0.0002</td>
<td>12 and 17</td>
</tr>
<tr>
<td>ALD NiO$_2$ film$^i$</td>
<td>~330</td>
<td>896 ± 206</td>
<td>0.17 ± 0.04</td>
<td>37</td>
</tr>
<tr>
<td>2-3 nm IrO$_2$ layer</td>
<td>350</td>
<td>—</td>
<td>0.046</td>
<td>7</td>
</tr>
<tr>
<td>2-3 nm Ni$<em>{0.85}$Fe$</em>{0.15}$O$_3$</td>
<td>—</td>
<td>—</td>
<td>0.4-0.6</td>
<td>7</td>
</tr>
<tr>
<td>NiFe LDH</td>
<td>430</td>
<td>15 ± 8.7</td>
<td>0.0089 ± 0.005</td>
<td>36</td>
</tr>
<tr>
<td>NiFe LDH/CNT</td>
<td>~330</td>
<td>1065 ± 129</td>
<td>0.21 ± 0.03</td>
<td>19</td>
</tr>
<tr>
<td>NiFe LDH/CNT</td>
<td>300</td>
<td>—</td>
<td>0.05</td>
<td>35</td>
</tr>
<tr>
<td>NiFe LDH/CNT</td>
<td>~250</td>
<td>—</td>
<td>0.56</td>
<td>1 and 7</td>
</tr>
<tr>
<td>BSCF</td>
<td>~240</td>
<td>—</td>
<td>0.0915</td>
<td>33</td>
</tr>
<tr>
<td>Monolayer Co</td>
<td>240</td>
<td>—</td>
<td>~0.6</td>
<td>34</td>
</tr>
<tr>
<td>FeOOH/Co/FeOOH</td>
<td>—</td>
<td>—</td>
<td>&lt;0.48</td>
<td>38</td>
</tr>
</tbody>
</table>

$a$ at 10 mA cm$^{-2}$. $b$ at $\eta = 300$ mV. $^*\text{in Fe-rich 1 M NaOH.}$

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spots, and thus minimize local damage to the Ni(OH)₂ nanosheets. Similarly, the 1.4 nm Ni(OH)₂ nanosheet also showed good stability under continuous reaction in an Fe-rich electrolyte, as shown in Fig S11.†

Conclusions

To conclude, we reported a wafer-scale 1.4 nm Ni(OH)₂ nanosheet fabricated by ILE. The Ni(OH)₂ nanosheet achieved significantly higher OER catalytic performance compared to thicker Ni(OH)₂ layers owing to the very large surface atom ratio and ultra-small cross-plane charge diffusion length. At \( \eta = 300 \text{ mV} \), the 1.4 nm Ni(OH)₂ nanosheet delivered a TOF value of 1.12 s⁻¹, which was over 3.6, 120 and 450 times higher than those of the 7.0 nm Ni(OH)₂ layers, 230 nm Ni(OH)₂ layers, and commercial RuO₂, respectively. By adding Fe salt into the electrolyte, the TOF further reached up to 5.47 s⁻¹ at \( \eta = 300 \text{ mV} \), which was ~2 orders of magnitude higher than those of typical OER catalysts. Due to the uniform thickness across the entire wafer area, the Ni(OH)₂ nanosheet also exhibited excellent operational stability. This is the first report of a wafer-scale ultrathin Ni(OH)₂ nanosheet, which exhibited drastically enhanced electrochemical catalytic activity. This work offers a promising new catalyst solution for water splitting. The ILE technology for synthesizing wafer-scale oxide 2D nanomaterials is exceptionally valuable for developing catalysts with unprecedented mass activity from rare and precious catalyst materials.

Conflicts of interest

There are no conflicts to declare.

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Notes and references


