Electronic Supplementary Information

Experimental and theoretical insight into sustained water splitting with electrodeposited nanoporous nickel hydroxide@nickel film as a electrocatalyst

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Experimental Section

Materials

Carbon cloth (CC) was provided by Hongshan District, Wuhan Instrument Surgical Instruments Business. NiSO$_4$·6H$_2$O, Ni(NO$_3$)$_2$·6H$_2$O, and KOH were purchased from Aladdin Ltd. (Shanghai, China). Pt/C (20 wt% Pt on Vulcan XC-72R), Nafion (5 wt%), and RuCl$_3$·xH$_2$O were purchased from Sigma-Aldrich. The water used throughout all experiments was purified through a Millipore system.

Preparation of Ni(OH)$_2$@Ni/CC

Typically, the electrodeposition process was carried out in a three-electrode cell using CC or Ni(OH)$_2$/CC as the working electrode, a graphite plate as the counter electrode, and Ag/AgCl (3 M KCl) as the reference electrode. Ni(OH)$_2$ was directly
electrodeposited on a piece of CC (1 cm × 2 cm) from 0.1 M Ni(NO$_3$)$_2$ aqueous solution at a constant potential of -1.0 V (vs. the saturated calomel electrode (SCE)) for 420 s at 25 °C. Then, Ni was electrodeposited on the surface of Ni(OH)$_2$/CC by performing cyclic voltammogram for 20 cycles at a sweep rate of 50 mV s$^{-1}$ in 0.1 M NiSO$_4$·6H$_2$O aqueous solution. After deposition, the Ni(OH)$_2$@Ni/CC was removed from the cell, rinsed with deionized water for several times, and dried by nitrogen flow. The reference sample, Ni/CC was prepared through the similar method to Ni(OH)$_2$@Ni/CC using the CC as the working electrode. The loading for Ni(OH)$_2$@Ni on CC was determined to be 2.8 mg cm$^{-2}$ with the use of a high precision microbalance.

The Ni@Ni(OH)$_2$/CC electrode was also prepared by electrodeposition of Ni(OH)$_2$ on the surface of Ni/CC substrate for the comparison purpose.

**Characterizations**

Powder XRD data were acquired on a RigakuD/MAX 2550 diffractometer with Cu Kα radiation ($\lambda$=1.5418 Å). SEM measurements were carried out on a XL30 ESEM FEG microscope at an accelerating voltage of 20 kV. XPS measurements were performed on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source. TEM measurements were performed on a HITACHI H-8100 electron microscopy (Hitachi, Tokyo, Japan) with an accelerating voltage of 200 kV.

**Electrochemical measurements**

All the electrochemical measurements were conducted using a CHI660E potentiostat (CH Instruments, China) in a typical three-electrode setup, using a piece
of freshly made Ni(OH)$_2$@Ni/CC as the working electrode, a graphite rod as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. Pt/C and RuO$_2$ were loaded on CC (mass loading: 2.8 mg cm$^{-2}$) for comparison, respectively. Prior to measurement, a resistance test was made and the iR compensation was applied to all initial data for further analysis. EIS measurements were carried out in the frequency range of 100 kHz–0.1 Hz. In all measurements, the SCE reference electrode was calibrated with respect to RHE. In 1.0 M KOH, E (RHE) = E (SCE) + 1.067 V. LSV curves were conducted in electrolyte with scan rate of 5 mV s$^{-1}$ without any activation. The long-term durability test was performed using chronopotentiometric measurements. All the potentials reported in our work were expressed vs. the RHE.

**Computational Section**

All calculations were performed in this study using density functional theory (DFT) with the program package of DMol3$^{[S1,S2]}$ in the Materials Studio of BIOVIA Inc. The exchange-correlation energy was described by local functionals (LDA) using the PWC$^{[S3]}$ function. All electron relativistic and polarization double numerical basis-set (DNP) was employed to all elements. DFT simulations were performed based on the experimentally crystal structure$^{[S4]}$ of Ni(OH)$_2$ (ICSD collection code: 109391). A charge density mixing of 0.01 was used to all calculations. Previous surface morphology study$^{[S5]}$ showed that the 110 is one favor surface, which was further used for investigating Ni(OH)$_2$ active surface. Chemisorption surfaces were constructed as slab consists of eight layers in 3 × 3 super cells, which separated by 20
Å vacuum. The Monkhorst-Pack\cite{S6} sampling scheme with $5 \times 3 \times 3$ was used for Ni(OH)$_2$ geometrical optimization. And a $3 \times 3 \times 1$ sampling scheme was used to calculate all the interaction energies. All calculations were performed with spin-polarization.

It is important to make sure that the surfaces structures we create are stable enough for catalyzing HER reaction, and thus the study of surface energy is necessary. The formula used for calculating surface energy is as below:

$$\gamma_{surf} = \frac{1}{2A_0} \left( E_{slab} - \sum N_i \mu_i \right)$$

Where, $\gamma_{surf}$ is the surface energy, $E_{slab}$ is the total surface slab energy, $N_i$ is the numbers of the corresponding atoms in the surface, $\mu_i$ is the chemical potentials of the corresponding type of atoms.

Previous studies showed that the hydrogen evolution activity is strongly correlated with the free energy of hydrogen to the electrocatalyst surface.\cite{S7,S8} The free energy change for H* adsorption on Ni, Ni(OH)$_2$ and Ni(OH)$_2$@Ni surfaces ($\Delta G_H$) was calculated as follows, which is proposed by Norskov and coworkers\cite{S9}:

$$\Delta G_H = E_{total} - E_{sur} - E_{H2}/2 + \Delta E_{ZPE} - T\Delta S$$

where $E_{total}$ is the total energy for the adsorption state, $E_{sur}$ is the energy of pure surface, $E_{H2}$ is the energy of H$_2$ in gas phase, $\Delta E_{ZPE}$ is the zero-point energy change and $\Delta S$ is the entropy change.
Fig. S1 XPS spectra in the (a) Ni 2p and (b) O 1s regions for Ni(OH)$_2$@Ni/CC.
Fig. S2 (a) XRD pattern and (b, c, d) SEM images of Ni(OH)$_2$/CC.
Fig. S3 (a) N$_2$ adsorption-desorption isotherm and (b) pore size distribution of Ni(OH)$_2$@Ni/CC.
Fig. S4 (a) XRD pattern and (b, c) SEM images of Ni/CC.
Fig. S5 Polarization curves for Ni(OH)$_2$/CC with different electrodeposition time in 1.0 M KOH with a scan rate of 5 mV s$^{-1}$. 

Current density (mA cm$^{-2}$) vs. Potential (V vs. RHE) for different electrodeposition times.

- 300 s
- 420 s
- 540 s
Fig. S6 Polarization curves for Ni(OH)$_2$@Ni/CC and Ni@Ni(OH)$_2$/CC in 1.0 M KOH with a scan rate of 5 mV s$^{-1}$.
Fig. S7 CVs for (a) Ni(OH)$_2$@Ni/CC, (b) Ni/CC, and (c) Ni(OH)$_2$/CC.
Fig. S8 (a, b) SEM images of Ni(OH)$_2$@Ni/CC after 1000 cycles of continuous cyclic voltammetry.
Fig. S9 XPS spectrum in Ni 2p region for Ni(OH)$_2$@Ni/CC after 1000 cycles of catalytic reaction.
Fig. S10 (a) Polarization curves and (b) Nyquist plots for Ni(OH)$_2$@Ni/CC with electrodeposition of Ni on Ni(OH)$_2$/CC at different duty cycles in 1.0 M KOH with a scan rate of 5 mV s$^{-1}$. 
Fig. S11 (a, b) SEM images of Ni(OH)$_2$@Ni/CC after 20 h of bulk water electrolysis in 1 M KOH.
In order to check the validity of Ni electrodeposited on the surface of Ni(OH)$_2$, estimate the layer number of bulk-like slabs Ni is necessary. Four-, five-, and six-layer Ni(OH)$_2$ slabs were examined and the results of corresponding surface energy were showed in table S1. The calculations of surface energy for Ni(OH)$_2$ slabs converge to a fixed value, 2.01×10$^{-3}$ hartree/Å$^2$, when it contains more than five layers. Therefore, the slab with five layers is considered to be stable in this paper, which was further used to be the basal for covering Ni atoms. Similarly, the number of Ni layers which covered on Ni(OH)$_2$ slabs were also estimated. Two-, three-, four-, and five-layer Ni cover on Ni(OH)$_2$ slabs were examined (table S2) and the surface energy of Ni layers converges to an approximate fixed value 224.67 hartree/Å$^2$. The energies will become close because the Ni layer will be reconstructed, as demonstrates in Fig. S10. For taking all possibility into consideration, five-layer Ni covered on the surface of Ni(OH)$_2$ was the optimized condition for our study.

Table S1. The surface energy ($\gamma$) of Ni(OH)$_2$ with respect to the number of layers.

<table>
<thead>
<tr>
<th>Number of layers, N</th>
<th>Surface energy (hartree/Å$^2$)</th>
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<tbody>
<tr>
<td>4</td>
<td>2.43×10$^{-3}$</td>
</tr>
<tr>
<td>5</td>
<td>2.01×10$^{-3}$</td>
</tr>
<tr>
<td>6</td>
<td>2.01×10$^{-3}$</td>
</tr>
</tbody>
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Table S2. The surface energy ($\gamma$) of Ni(OH)$_2$@Ni with respect to the number of Ni layers.

<table>
<thead>
<tr>
<th>Number of Ni cover layers, N</th>
<th>Surface energy (hartree/Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>244.88</td>
</tr>
<tr>
<td>3</td>
<td>244.70</td>
</tr>
<tr>
<td>4</td>
<td>244.67</td>
</tr>
<tr>
<td>5</td>
<td>244.67</td>
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</tbody>
</table>
Fig. S12 The origin and reconstructed (a) two-, (b) three-, (c) four-, and (d) five-Ni layers covered on the Ni(OH)$_2$.

References


