Supporting Information

Single-Crystalline Ultrathin Nickel Nanosheets Array from In Situ Topotactic Reduction for Active and Stable Electrocatalysis
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Experimental Details

Synthesis of Ni(OH)$_2$ nanowalls: Ni(OH)$_2$ nanowall films were synthesized following our previous report (Chem. Commun. 2011, 47, 9651). In a typical procedure, Ni(NO$_3$)$_2$·6H$_2$O (1.45 g, 5 mmol) and Hexamethylenetetramine (1.40g, 10 mmol) were dissolved in 35–38 mL distilled water and stirred to form a clear solution. Nickel foam (about 3.3 cm x 1 cm) was carefully cleaned with concentrated HCl solution (37 wt.%) in an ultrasound bath for 30 s in order to remove the surface oxide layer. And then deionized water and absolute ethanol were used for 10 min each to ensure the surface of the Ni foam was well cleaned. The aqueous solution and the Ni foam were transferred to a 40 mL Teflon-lined stainless-steel autoclave, which was sealed, maintained at 100 °C for 10 h, and then allowed to cool to room temperature within 15 minutes using cooling water. The thin nanosheets on the metal substrate were rinsed several times with distilled water and ethanol with the assistance of ultrasonication, and dried at 80 °C for 6 h.

Synthesis of the nickel nanosheet array through in situ reduction: In a typical procedure, NaOH (1 g ) and EG (36ml) were put into a 40 mL Teflon-lined stainless-steel autoclave, and stirred until solid dissolved. Then Ni(OH)$_2$ nanowall films were transferred to the Teflon-lined stainless-steel autoclave, maintained at 160 °C for 12 h for final products. The post treatment of Ni-NSA was similar to those of Ni(OH)$_2$ nanowalls except for the drying process. The Ni-NSA should be stored in the environment without oxygen to avoid oxidation.

Synthesis of the nickel nanoparticle assembly: Synthesis of nickel nanoparticle assembly following similar procedure as Ni-NSA but in a harsher reduction condition (1g NaOH, 180 °C) with the assistance of 1.5g NaBH$_4$.

Materials Characterization. X-ray diffraction (XRD) patterns were collected on Shimadzu XRD-6000 with Cu Kα radiation (40 kV, 30 mA, $\lambda = 1.5418\text{Å}$), recorded with 2θ ranging from 15° to 90°. Elemental analysis was investigated by inductively coupled plasma optical emission spectrometry (ICP-OES; Thermo Scientific iCAP 6300). The morphologies of as-synthesized samples were characterized by transmission electron microscopy (TEM; FEI G$^2$ 20) and high-resolution transmission electron microscopy (HRTEM; JEOL, JEM-2100, 200 kV).

It should be noted that ultrathin 2D nanostructure made Ni nanosheets sensitive to oxygen in the ambient atmosphere and electron beam during the TEM characterization. Therefore, the Ni nanosheets must be kept at inert atmosphere before TEM characterization and electron exposures employed must be very low during electron microscopy to minimize irradiation damage.

Note on ICP tests: we used the Ni nanostructures grown on copper foam for ICP test. To ensure that Ni(OH)$_2$ have essentially the same growth behavior on both Ni and Cu foam, we did another control experiment. That is, we grew the NiFe layered double hydroxides under exactly the same condition on both the nickel and copper foam, by analyzing the Fe contents of the two samples after growth through ICP, we found that the massloading values were almost the same. Since Ni(OH)$_2$ has similar structure.
to NiFe layered double hydroxides, we believed that Ni(OH)$_2$ grown on nickel and copper foams have the same mass loading, therefore, we used the ICP result of Ni nanosheets array grown on copper foam instead to estimate the amount of Ni NSA on Ni foam. The experimental details can be found at supporting information.

**DFT Calculation.** The DFT calculations are performed using a plane wave implementation at the generalized gradient approximation (GGA) PBE level. A full optimization of all atom positions in the bulk Ni was performed via the action of a conjugate gradient optimization procedure. The bulk lattice constants of Ni are optimized using the 5*5*5 Monkhorst–Pack type of k-point sampling. The cutoff energy was set to 400 eV, the energy change convergence criterion was 1×10$^{-5}$ eV. Atomic positions are relaxed until the sum of the absolute forces is less than 0.01 eV/Å$. All surface energies were calculated within GGA as defined above using a simulation cell size of 1 × 1 primitive cells. A minimal thickness of six Ni layers with 16 Å of vacuum was required to obtain convergence in the adsorption energies, the optimize geometries with one oxygen atom adsorbed on the (1*1) slab (1/4 ML) is considered to compare the hydrogen adsorption energies. The k-point sampling consists of 5×5×1 Monkhorst-Pack points for the slab model. During structure relaxation, both the adsorbents the top three Pt or Ni layers in the structure of the (111) surface were relaxed. The rest three below layers were kept frozen at their positions.

**Electrochemical Measurements.**
All electrochemical tests were performed in a standard three-electrode electrochemical cell with Pt foil (1 cm$^2$) and saturated calomel electrode (SCE) used as counter electrode and reference electrode at room temperature (~20 °C) using a Princeton P4000 electrochemical workstation. 1 cm * 1 cm area of Ni-NSA and Ni-NPA were used directly as working electrodes while Pt/C was loaded on Ni foam substrate as working electrodes. It should be noted that the loading amount of Pt/C was twice of Ni-NSA due to poor adhesion to substrate.
In the hydrazine oxidation reaction, Cyclic voltammetry and linear sweep voltammetry with scan rate of 5 mV·s$^{-1}$ were conducted in 3 M KOH solution with different hydrazine concentrations. AC impedance measurements were carried out in the same configuration at -1.0 V vs. RHE from 10$^{-1}$ to 10$^{5}$ Hz with an AC voltage of 5 mV. The stability tests were operated at high overpotentials to achieve high initial current densities.
Prior to the HER test measurements, H$_2$ was bubbled through the electrolyte solution to eliminate the dissolved oxygen and to maintain a fixed Nernst potential for the H$^+$/H$_2$ redox couple. Linear sweep voltammetry with scan rate of 5 mV/s was conducted in 0.1 M and 1 M KOH solution. AC impedance measurements were carried out in the same configuration at -0.2 V vs. RHE in the frequency range of 10$^{-1}$ to 10$^{5}$ Hz with an AC voltage of 5 mV. The stability tests were operated at high overpotentials to achieve high initial current densities.

**Supplementary Figures**
Figure S1. SEM image and XRD pattern of Ni-NSA grown on Cu foam substrate. The strong peaks were generated from Cu substrate. The red and blue lines indicated standard peaks of face centered cubic phased Cu and Ni respectively.

Figure S2 (A), (B), (D) TEM images of Ni nanosheets. (C) Electron Diffraction pattern of the region marked in (B). (E), (F) Electron Diffraction patterns of the regions marked in (D).
In order to reveal the topotactic conversion mechanism, we have carefully characterized the intermediates (0h, 3h, 6h, 9h and 12h samples) using HRTEM, electron diffraction and XRD. All the intermediates were first laid on carbon nanotube supported TEM grids, so it is possible to reveal the thickness change by observing the cross-sections of verticle laid nanosheets. It is could be seen in
column 1 that the thickness was changed from ~6 nm to 4–5 nm (3h) to 3–4 nm (6h) to 2–3 nm (9h) to ~2 nm (12h) during the topotactic conversion process. It should be noted that focusing the electron beams on Ni(OH)₂ would immediately cause dehydration, so only under low beam density and low magnification the vertical laid nanosheets could be kept stable and the thicknesses could be observed. That is why the intermediates were not as clear as the final products.

TEM on the basal planes of the intermediates (column 2) revealed the morphology variation. It could be seen the nanosheets of 3h sample began to wrinkle while 6h sample showed severe folding state, which is possibly caused by the crystal lattice mismatch between Ni(OH)₂/NiO/Ni. However, from 9h to 12h the wrinkling was weakened and finally thin flat nanosheets formed.

Electron diffraction (ED) was also applied to reveal crystalline evolution during the topotactic conversion. It could be seen that the starting material was pure β-phase hexagonal Ni(OH)₂, which was in good agreement with XRD pattern (Figure 1A in the manuscript). After 3 hours’ reaction, the 1/3 (422) crystalline lattice of cubic phased NiO appeared on the ED pattern, possibly due to the dehydration of Ni(OH)₂ happened on the high temperature/pressure environment. But at this stage no Ni was observed, suggesting no reduction happened. When the reaction stopped at 6h, the NiO pattern was strengthened and 1/3 (422) crystalline lattice of fcc Ni appeared, revealing that the reduction of Ni(OH)₂ to Ni experienced a phase transformation from hexagonal phased Ni(OH)₂ to cubic phased NiO followed by a reduction from cubic NiO to cubic Ni. As the reaction continues to 9h, Ni(OH)₂ disappeared on the ED pattern while Ni pattern was strengthened. It should be noted that there is no reaction stage showing NiO dominated ED pattern, possible because the reduction of NiO to Ni was a quick reaction and dehydration was the kinetic control step. At the final stage (12h), the products exhibited pure fcc Ni pattern, demonstrating fully reduction.

![Figure S4. XRD patterns showing crystalline evolution of the topotactic conversion intermediates (3h, 6h, 9h, 12h)](image)

XRD patterns of the intermediates fit well with the crystalline structure evolution, as shown on the left. The 3h sample shows typical β-phase hexagonal Ni(OH)₂. From 3h to 6h, the Ni(OH)₂ pattern was weakened due to the dehydration. However, no NiO and Ni patterns were observed at this stage, possibly because the as formed NiO and Ni were very little for XRD detection. 9h sample shows typical fcc Ni diffraction peaks, demonstrating the reduction to Ni mainly happened at 6h to 9h time slot, which was coincide with electron diffraction results. From 9h to 12h, the Ni pattern was strengthened due to further topotactic conversion.
Figure S5. SEM images of (A) Ni(OH)$_2$ and (B)-(F) reduction products under different reduction temperature, with NaOH concentration kept at 0.625 M.

Figure S6. Adhesive forces measurements of the gas bubbles on Ni-NSA, Ni(OH)$_2$ nanosheet array, pure Ni foam and 20 Wt% Pt/C (loaded on Ni foam) electrodes, demonstrating that Ni-NSA and Ni-NPA afford an extremely small bubble adhesive force and underwater “superaerophobic” surface.
Figure S7. SEM image of Ni nanoparticle assembly (Ni-NPA) prepared in 0.625M NaOH and 1M NaBH₄ solution at 180°C, much harsher conditions than those required for Ni-NSAs.

Figure S8. HzOR Stability test of Ni-NSA at different current densities. Only ~8.2%, 6.4% and 4.3% losses were observed for each condition.
Figure S9. SEM image of Ni-NSA before and after HzOR or HER stability tests

Figure S10. XPS of Ni/NiO-NSA grown on Cu substrate with partial oxidation in vacuum oven (~1x10^3 Pa) for 6h
Figure S11. Tafel plots Ni-NSA and 20 Wt% Pt/C for HER in 0.1M KOH.

Figure S12. HER stability tests of Ni/NiO-NSA and Pt/C. Much smaller loss of Ni/NiO-NSA (5.1%) than Pt/C (13.3%) indicated much higher stability.