Electronic Supplementary Information

Confined carburization-engineered synthesis of ultrathin nickel oxide/nickel

heterostructured nanosheets for enhanced oxygen evolution reaction

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Table S1. Comparison of OER electrocatalytic performance between this work and other previously

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References

Experimental section

Chemicals and materials: Nickel acetate tetrahydrate ($C_4H_6NiO_4\cdot 4H_2O$), ethanol (C_2H_5OH), cetyltrimethyl ammonium bromide (CTAB), dopamine hydrochloride ($C_8H_{11}NO_2\cdot HCl$), ammonium hydroxide (NH₄OH), and potassium hydroxide (KOH) were used in the experiments. The deionized water (DI water) used in the experiments was from local sources.

Synthesis of ultrathin Ni(OH)₂ nanosheets: The ultrathin β -Ni(OH)₂ nanosheets were synthesized through a facile solvothermal method according to previous reports with minor modification.^{S1} Firstly, 2.2 g CTAB and 2.4 mmol C₄H₆NiO₄·4H₂O were added into a mixed solution of 60 mL ethanol and 11 mL DI water. After being stirred for 1 h, the homogenous solution was transferred into 100 mL stainless-steel autoclave lined with polytetrafluoroethylene (PTFE) and heated at 180 °C for 24 h. The final light green product was collected by centrifugation, washing with water and ethanol thoroughly, followed by vacuum drying.

Synthesis of Ni(OH)₂@**PDA nanosheets:** Polydopamine (PDA) was in-situ synthesized onto the surface of Ni(OH)₂ nanosheets in air atmosphere. 150 mg as-prepared Ni(OH)₂ nanosheets were first dispersed into 150 mL DI water under sonication for 50 min. Then, 300 mg dopamine hydrochloride were dissolved into 60 mL DI water and dropwise added into the as-prepared Ni(OH)₂ solution. The mixed solution was kept stirring at 25 °C for 15 min, 60 min, and 120 min for the different amount of PDA coating. Finally, the resultant product (denoted as Ni(OH)₂@PDA-15, Ni(OH)₂@PDA-60, and Ni(OH)₂@PDA-120, respectively) was collected via centrifugation and being washed three times with DI water and ethanol, respectively, followed by vacuum freeze-drying.

Synthesis of NiO_x/Ni nanosheets: The as-prepared 2D core-shell Ni(OH)₂@PDA nanosheets were annealed at 600 °C for 2 h in N₂ flowing with a heating rate of 5 °C min⁻¹ to yield the NiO_x/Ni nanosheets (denoted as NiO_x/Ni-15, NiO_x/Ni-60, and NiO_x/Ni-120 derived from Ni(OH)₂@PDA-15, Ni(OH)₂@PDA-60, and Ni(OH)₂@PDA-120, respectively). The synthesis procedure of pure NiO_x was same as that of NiO_x/Ni samples expect using pure Ni(OH)₂ nanosheets to replace the Ni(OH)₂@PDA counterpart.

Synthesis of N-doped carbon spheres: 0.75 mL NH₄OH was added into the mixture of 40 mL ethanol and 90 mL DI water, and then 500 mg dopamine hydrochloride was dissolved into 10 mL DI water and added into the above solution for stirring 24 h. Finally, the PDA spheres were collected by centrifugation, washed with water and ethanol thoroughly, followed by vacuum drying. The PDA spheres were annealed at 600 °C for 2 h in N₂ flowing with a heating rate of 5 °C min⁻¹ to obtain the N-doped carbon spheres.

Characterizations: A Hitachi New Generation cold field emission SEM SU-8010 spectrophotometer was applied to determine field-emission scanning electron microscopy (FESEM). The samples were uniformly dispersed on the Si platelets for the tests. Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), and elements mapping analysis were conducted using a JEM-2100 EX instrument at an accelerating voltage of 200 kV. Atomic force microscopy (AFM) spectra were measured by a Nanoscope IIIA system and samples were dispersed on the mica plates for the tests. Raman measurement was performed on a NTEGRA Spectra system (NT-MDT) with a wavelength of 532 nm. X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance powder diffractometer. An AXIS Ultra DLD system was employed for X-ray photoelectron spectroscopy (XPS). The depth XPS spectrum was conducted via argon sputtering (3 kV, 2 µA energy). All binding energies were calibrated by the C 1s peak at 284.6 eV. Thermogravimetric analysis was operated *via* a TA SDT 2960 thermoanalyzer.

Electrochemical tests: Electrochemical measurements were carried out with a three-electrode system on an electrochemical workstation (CH Instruments 760E). A glassy carbon electrode (3 mm in diameter, 0.07 cm²) coated with various catalysts was applied as the working electrode. An Ag/AgCl electrode and a graphite rod were used as the reference electrode and counter electrode, respectively. The electrolyte was 1 M KOH. Typically, 5 mg as-synthesized catalyst combined with carbon black were dissolved in a mixture of 50 µL Nafion solution (5 wt%) and 450 µL ethanol under sonication for 2 h to form a homogeneous ink. Subsequently, 2.0 uL ink was drop-casted onto the surface of the glassy carbon electrode with a mass loading of 0.286 mg cm⁻². Before the measurements of electrochemical properties, the catalysts were activated with numerous cyclic voltammetry (CV) cycles until they were stable. Linear sweep voltammetry was carried out from 0 to 0.8 V vs. Ag/AgCl with a scan rate of 5 mV s⁻¹. All polarization curves were presented with iR correction. The electrochemical impedance spectroscopy (EIS) test of samples was performed at a potential of -0.65 V vs. Ag/AgCl. The double-layer capacitance (C_{dl}) was measured by CV cycling from 0 to 0.1 V vs. Ag/AgCl at sweep rates of 20–120 mV s⁻¹ in 1 M KOH. The chronoamperometry curves was conducted to test the stability. The catalyst was drop-casted onto the Ni foam (10 mm \times 10 mm) with a mass loading of 1.0 mg cm⁻². All potentials were normalized to the reversible hydrogen electrode (RHE) according to the Nernst equation: $E_{(vs. RHE)} = E_{(vs. Ag/AgCl)} + 0.0591 V \times pH$ + 0.197 V.

In addition, the overall water splitting device driven by solar cells was conducted in a twoelectrode system. For the two-electrode HER-OER device, the cathode was NiO_x/Ni (1.0 mg cm⁻²) loaded on Ni foam (10 mm × 10 mm); and the anode was commercial Ir/C (1.0 mg cm⁻²) loaded on Ni foam (10 mm × 10 mm).



Fig. S1 Oxidation mechanism of the formation of PDA.

Note: The polymerization process of dopamine to PDA generally reacts under alkaline conditions.^{S2} As the oxidation mechanism of the formation of PDA shown in Fig. S1, the protons generated from the oxidation process would be consumed under alkaline conditions, and thus the equilibrium would shift toward the product.^{S3}



Fig. S2 Schematic illustration for in-situ synthesis of Ni(OH)₂@PDA nanosheets.

Note: As reported in literatures, the Tris-buffer solution or ammonia solution was applied to create an alkaline condition for the polymerization process of dopamine. In this work, the hydroxyl group (OH^{-}) was dissociated from ultrathin Ni $(OH)_2$ itself to form a local alkaline condition in the solution, and the oxygen dissolved in solution served as an oxidizing agent to drive the in-situ polymerization process. In comparison to previous methods by adding inorganics/organics to create an alkaline condition, this synthesis method is distinguished by introducing no additives to proceed polymerization, which is facile and more controllable.



Fig. S3 AFM image of Ni(OH)₂ nanosheet with corresponding height profile.



Fig. S4 Enlarged TEM image.

Note: Such enlarged TEM image demonstrated the Moiré pattern of the overlapped ultrathin Ni(OH)₂ nanosheets.



Fig. S5 SEM images of (A) Ni(OH)₂@PDA-15 and (B) Ni(OH)₂@PDA-120 (insets: SEM images of side faces).



Fig. S6 Photographs of blank Ni(OH)₂ nanosheets and the corresponding Ni(OH)₂@PDA with different polymerization time of dopamine (15 min, 60 min, and 120 min).



Fig. S7 (A, B) SEM images of NiO_x/Ni-15. (C) TEM image of NiO_x/Ni-15.



Fig. S8 (A, B) SEM images of NiO_x/Ni-120. (C) TEM image of NiO_x/Ni-120.



Fig. S9 Additional TEM image of NiO_x/Ni-60 nanosheets.

Note: The TEM image demonstrated the Moiré patterns of the overlapped ultrathin $NiO_x/Ni-60$ heterostructured nanosheets. The Moiré patterns were indexed by yellow arrows.



Fig. S10 (A) SEM image and (B) TEM image of NiO_x nanosheets.



Fig. S11 AFM image of NiO_x nanosheets with corresponding height profiles.



Fig. S12 XRD patterns and partially enlarged XRD patterns of $NiO_x/Ni-15$, $NiO_x/Ni-60$, and $NiO_x/Ni-120$. The intensity was normalized.



Fig. S13 SEM images of (A) PDA spheres and (B) N-doped carbon spheres. (C) XRD pattern of N-doped carbon spheres.

Note: As shown in Fig. S13A, the PDA nanospheres were quite uniform. After calcination, the N-doped carbon spheres was obtained with uniform diameter of about 300 nm (Fig. S13B). The XRD pattern of the N-doped carbon spheres showed a broad peak at about 25°, assigned to the (002) diffraction mode characteristic of a carbonaceous structure (Fig. S13C).^{S4}



Fig. S14 Raman spectra of NiO_x/Ni-60 collected by Raman mapping on an area of about 35 μ m × 35 μ m.

Note: The three peaks are detected at ~500, 1094, and 1388 cm⁻¹, corresponding to longitudinal optical (LO), 2LO and two magnon (2M) of NiO. No characteristic peaks of carbonaceous materials were detected, indicating no carbonaceous materials within a wide range of the tested samples.



Fig. S15 HRTEM image of NiO_x.



Fig. S16 Additional HRTEM image of the edge of NiO_x/Ni -60 nanosheet.



Fig. S17 HAADF-STEM image of NiO_x/Ni -60 and the corresponding EDX elemental mappings.



Fig. S18 XRD patterns of $NiO_x/Ni-60$ under different states: fresh and storage in N_2 and air atmosphere for two weeks, respectivily. The intensity was normalized.

Note: The fresh samlpe was tested immediately after calcination treatment. The other two samples were stored in N_2 and air atmosphere for two weeks, respectively. The intensity of Ni peaks for these samples was negligibly changed, indicating that the metallic Ni was restrained to be oxidized. Therefore, it can be reasonably concluded that the metallic Ni located in the interior of the heterostructured nanosheets instead of on the surface due to the high oxidability in the presence of oxygen.



Fig. S19 Depth N 1s XPS spectra for NiO_x/Ni-60 after Ar ion etching at different periods of time.



Fig. S20 TGA curves with a heating rate of 5 °C min⁻¹ from room temperature to 800 °C under N_2 atmosphere for Ni(OH)₂@PDA-60, Ni(OH)₂, and PDA sphere.

Note: The TGA results showed that the dehydration process of Ni(OH)₂ into NiO_x occurred at 290-310 °C. The weight loss trend of Ni(OH)₂@PDA-60 was almost identical to that of Ni(OH)₂, indicating that the Ni(OH)₂ was also successfully transformed into NiO_x with the coating of PDA. Compared with that of NiO_x, the slight postponed time for the weigh loss of Ni(OH)₂@PDA-60 at 295 °C might be ascribed to the decomposition of of PDA coating as an endothermic reaction.



Fig. S21 Schematic illustration of the carburization reaction.



Fig. S22 Mass activities at an overpotential of 400 mV for $NiO_x/Ni-60$, $Ni(OH)_2$, NiO_x , and Ir/C, respectively.



Fig. S23 (A) Polarization curves of $NiO_x/Ni-15$, $NiO_x/Ni-60$, and $NiO_x/Ni-120$. (B) The corresponding Tafel plots derived from the polarization curves in (A).



Fig. S24 CV curves of the (A) $NiO_x/Ni-60$, (B) $Ni(OH)_2$, and (C) NiO_x collected at 20, 40, 60, 80, 100, and 120 mV s⁻¹ in 1.0 M KOH solution.



Fig. S25 CV curves of the (A) $NiO_x/Ni-15$ and (B) $NiO_x/Ni-120$ collected at 20, 40, 60, 80, 100, and 120 mV s⁻¹ in 1.0 M KOH solution.



Fig. S26 Double-layer capacitance (C_{dl}) of NiO_x/Ni-15, NiO_x/Ni-60 and NiO_x/Ni-120.



Fig. S27 ECSA-normalized polarization curves of NiO_x/Ni-15, NiO_x/Ni-60, NiO_x/Ni-120, Ni(OH)₂, and NiO_x.

Note: The C_{dl} can be converted into an electrochemical active surface area (ECSA) using the specific capacitance value for a flat standard with 1 cm² of real surface area. The specific capacitance for a flat surface is generally found to be in the range of 20-60 µF cm⁻².^{S5} Here, we assumed it as 40 µF cm^{-2} .

The calculated ECSA of NiO_x/Ni-15:

$$A_{ECSA} = \frac{2.96 \text{ mF cm}^{-2}}{0.04 \text{ mF cm}^{-2} \text{ per cm}_{ECSA}^{2}} = 74 \text{ cm}_{ECSA}^{2}$$

$$A_{ECSA} = \frac{4.65 \text{ mF cm}^{-2}}{0.04 \text{ mF cm}^{-2} \text{ per cm}_{ECSA}^{2}} = 116.25 \text{ cm}_{ECSA}^{2}$$

The calculated ECSA of NiO_x/Ni-120:

The calculated ECSA of Ni(OH)₂

The calculated ECSA of NiO_x:

$$A_{ECSA} = \frac{4.65 \ mF \ cm^{-2}}{0.04 \ mF \ cm^{-2} \ per \ cm_{ECSA}^{-2}} = 116.25 \ cm_{ECSA}^{-2}$$

$$A_{ECSA} = \frac{4.16 \, mF \, cm^{-2}}{0.04 \, mF \, cm^{-2} \, per \, cm_{ECSA}^{2}} = 104 \, cm_{ECSA}^{2}$$

$$A_{ECSA} = \frac{2.21 \, mF \, cm^{-2}}{0.04 \, mF \, cm^{-2} \, per \, cm_{ECSA}^{-2}} = 55.25 \, cm_{ECSA}^{-2}$$

$$A_{ECSA} = \frac{1.98 \ mF \ cm^{-2}}{0.04 \ mF \ cm^{-2} \ per \ cm_{ECSA}^{-2}} = 49.5 \ cm_{ECSA}^{-2}$$



Fig. S28 (A) TEM and (B) HRTEM images of NiO_x/Ni-60 after stability test.

Note: It was observed from Fig. S28A that the ultrathin porous nanosheet structure was wellmaintained after stability test. Additionally, the overlapped nanosheets presented typical Moiré patterns (Fig. S28B). Therefore, those TEM results indicated a good structural robustness of the 2D ultrathin NiO_x/Ni heterostructure.



Fig. S29 XRD patterns of carbon black and NiO_x/Ni-60 before and after stability test.

Note: Besides the diffraction peak from carbon black, the diffraction peaks of $NiO_x/Ni-60$ after stability test were identical with those of pristine $NiO_x/Ni-60$, indicating it is a robust OER catalyst with good phase stability.



Fig. S30 XPS spectra of Ni 2p for NiO_x/Ni-60 before and after stability test.

Note: The percentage of Ni³⁺ after stability test was larger than that before reaction, revealing that some Ni²⁺ converted to Ni³⁺. This result could be contributed to the formation of amorphous NiOOH on the surface, which is consistant with the reported literatures.^{S6,S7}



Fig. S31 Image of the experimental devices for the light ON/OFF current measurements and the stability test of $Pt/C||NiO_x/Ni$ electrolyser driven by solar cell.

Note: The solar cell was connected in series with electrochemical workstation to collect the tested current. Because the workstation possessed a big internal resistance, the tested current in the circuit was far more less than the presumed one under the provided voltage in laboratory.



Fig. S32 Light ON/OFF current measurements of $Pt/C||NiO_x/Ni|$ and Pt/C||Ir/C| under identical voltage stimulated by solar cell.

Table S1. Comparison of OER electrocatalytic performances between this work and other previously

 reported NiO-based electrocatalysts in the literatures.

| Catalyst | Substrate | Mass loading (mg cm ⁻²) | Electrolyte | Scan rate (mV s ⁻²) | Overpotential (vs. RHE) at 10 mA cm ⁻² | Tafel slop (mV dec ⁻¹) | Reference |
|--------------------------------------|--|--|---------------|---------------------------------------|---|---|---|
| NiO _x /Ni | Glassy carbon electrode (GCE) | 0.286 | 1 M KOH | 5 | 358 | 51 | This work |
| Fe–nitrogen– carbon sheets/NiO | Rotating disk electrode (RDE) | 0.24 | 0.1 M KOH | 10 | 390 | 76 | Angew. Chem. Int. Ed. 2015 , 54,10530-10534 |
| Ce-doped NiO | Carbon fiber paper (CFP) | 0.56 | 1.0 M KOH | 5 | 382 | 119 | <i>Adv. Funct. Mater.</i> 2018 , <i>28</i> , 1706056 |
| Ni-Co mixed oxide cages | RDE | - | 1.0 M NaOH | 10 | 380 | 50 | <i>Adv. Mater.</i> 2016 , 28, 4601-4605 |
| NiO/Fe | Fluorine- doped tin oxide (FTO) | - | 0.1 M KOH | 20 | 480 | 30 | <i>Adv. Energy Mater.</i> 2015 , <i>5</i> , 1500412 |
| NiO/Ni | Graphite electrode | 0.5 | 1 M KOH | 10 | 345 | 53 | J. Mater. Chem. A 2016, 4,9797-9806 |
| Ni foam/porous carbon/NiO | Ni foam | - | 0.1M KOH | 5 | 520 | - | Angew. Chem. Int. Ed. 2013 , 52, 5248 -5253 |

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