Supporting information

Low-Cost Ni/$BaCO_3$ Composite Electrodes via Phase Transformation for Highly Efficient Alkaline Hydrogen Evolution

Experimental section

1. Synthesis of Ba/NPN@x and Pt/C Electrode

Commercial Nickel Oxide (NiO, 99%) and Barium Carbonate ($BaCO_3$, 99%) were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). Commercial 20 wt% Pt/C supported on Vulcan XC-72R carbon black was purchased from Premetek Co., Ltd. and used as received.

In a typical procedure, NiO and $BaCO_3$ were physically mixed in a mass ratio of 20:1. To ensure homogeneous mixing, the mixture was thoroughly ground in an agate mortar for 1.5 h. The resulting powder was then compacted into a pallet with a mass of approximately 0.25 g and a diameter of 13 mm under a uniaxial pressure of 68 MPa.

The as-prepared sample was subjected to high-temperature sintering in a muffle furnace at 1000 °C for 2 h in the air. After natural cooling to room temperature, the sintered sample was transferred to a tube furnace and reduced in a hydrogen (H_2) atmosphere for 30 min at various temperatures ranging from 300 to 600 °C. Finally, the reduced sample was allowed to cool naturally to room temperature, yielding the target Ba/NPN@x electrode.

Commercial 20 wt% Pt/C was used as the benchmark catalyst for HER comparison. Typically, 5 mg of 20 wt% Pt/C catalyst was dispersed in a mixed solvent containing 250 μL of deionized water, 700 μL of ethanol, and 50 μL of 5 wt% Nafion solution. The mixture was ultrasonicated for 30–60 min to obtain a homogeneous catalyst ink. Before use, the ink was further shaken or briefly sonicated to ensure uniform dispersion.

Carbon paper was used as the substrate for Pt/C loading. Prior to catalyst coating, the carbon paper was rinsed with ethanol and deionized water, followed by drying at room temperature or at 60 °C. The exposed geometric area was controlled to be 0.25 cm^2. The Pt/C ink was drop-cast onto the defined area of the carbon paper. To ensure uniform coating and avoid ink overflow, the total ink volume of 25 μL was deposited in several steps, with 5 μL added each time. The electrode was dried after each deposition before the next aliquot was added.

Based on the ink concentration of 5 mg mL^{-1}, the total Pt/C loading on the carbon paper was 0.125 mg, corresponding to a Pt/C loading of 0.5 mg cm^{-2}. Since the commercial Pt/C catalyst contained 20 wt% Pt, the actual Pt loading was 0.025 mg on the 0.25 cm^2 electrode, corresponding to a loading of 0.1 mg Pt cm^{-2}. The obtained Pt/C-coated carbon paper was used as the benchmark electrode for HER measurements under the same electrochemical testing conditions as the Ba/NPN electrodes.

2. Characterization

The sample phases were identified via an X-ray diffractometer (XRD, Bruker D2 PHASER, Germany) with Cu Kα radiation and a Raman spectrometer (Thermo Fischer DXR, China). The microstructure and elemental mapping of monoliths were analyzed using a transmission electron microscopy (TEM, JEOL JEM 2100F, Japan) and a scanning electron microscope (SEM, FlexSEM 1000II, Japan) equipped with energy-dispersive X-ray spectroscopy (EDS). The particle of the samples were also measured from the SEM images by Nano Measurer Software.

3. Electrochemical measurements

All electrochemical measurements were conducted in 1 M KOH using a conventional three-electrode configuration on a CHI660E electrochemical workstation. The as-prepared Ba/NPN electrode was directly used as the working electrode with an exposed geometric area of 1 x 1cm^2. A carbon rod and an Hg/HgO electrode were used as the counter and reference electrodes, respectively. In all measurements, the Hg/HgO electrode underwent calibration to align with the reversible hydrogen electrode (RHE) with the Nernst equation: $E_{RHE} = E_{Hg/HgO} + 0.059 \times pH + 0.098$ (in 1 M KOH). Before HER measurements, the electrodes were activated via 60 cycles of cyclic voltammetry (CV) between -0.8 V and -1.6 V at a scan rate of 5 mV/s. Linear sweep voltammetry (LSV) curves were recorded at a scanning rate of 1 mV/s and all the polarization curves were 95% iR-corrected. Electrochemical impedance spectroscopy (EIS) experiments were conducted at a frequency range of 10^{-2} Hz–10^{5} Hz, maintaining a potential of -0.3 V vs RHE with an amplitude of 5 mV. To obtain the electrochemically active surface area (ECSA), CV curves were tested within the potential window of 0.3–0.4 V at various scan rates, allowing for the estimation of the double-layer capacitance (C_{dl}). The ECSA was calculated based on the formula : ECSA = C_{dl}/C_{s}, the capacitance per unit area (C_{s}) is generally assumed to be 0.04 mF cm^{-2}.[1]

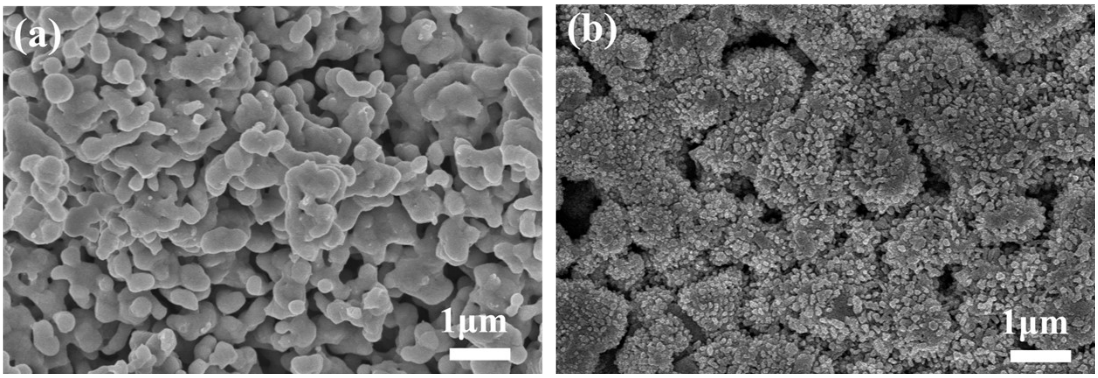

Figure S1. SEM images of (a) NiO reduced at 400 °C and (b) Ba/NPN@400.

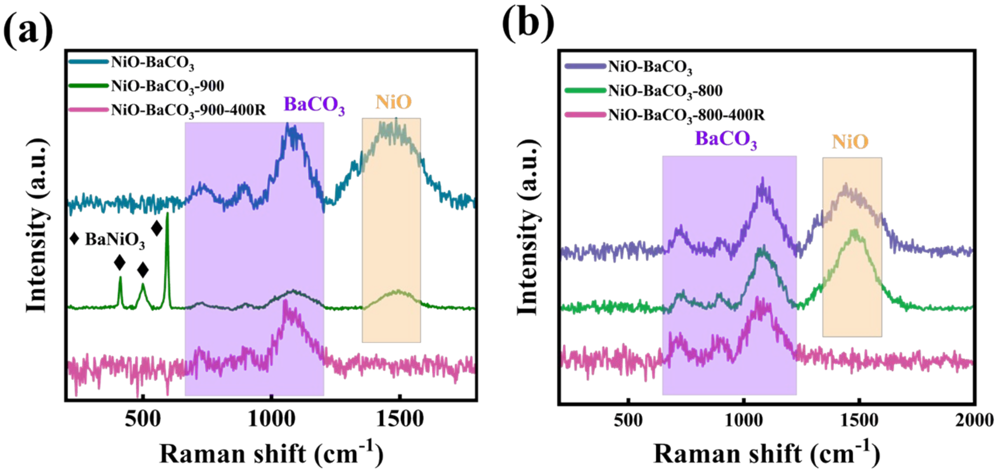

Figure S2. Raman spectra of the samples sintered at 900 °C and 800 °C.

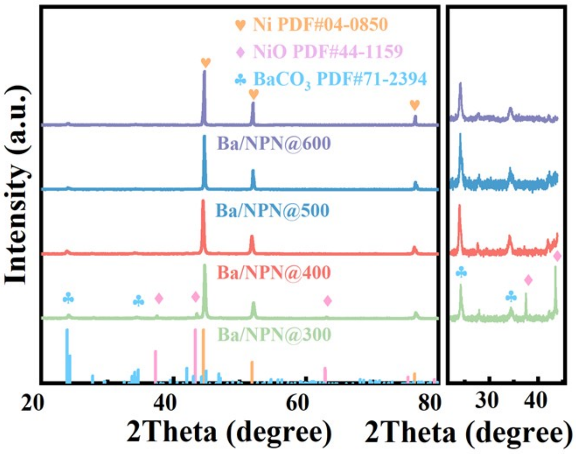

Figure S3. XRD patterns of Ba/NPN@x (x = 300, 400, 500, 600).

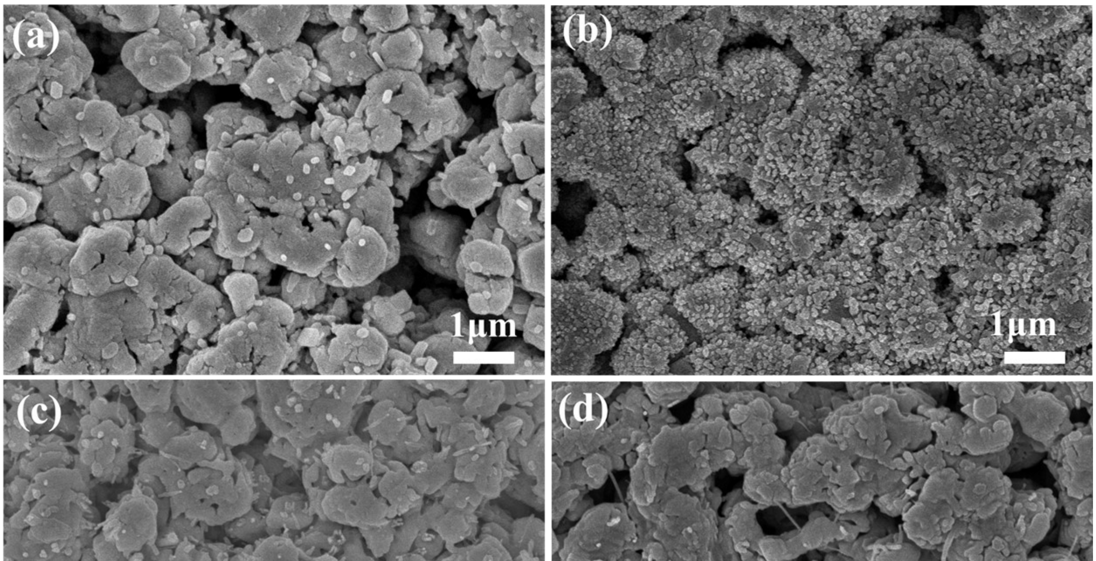

Figure S4. SEM images of samples at different reduction temperatures: (a) 300 ℃, (b) 400 ℃, (c) 500 ℃, (d) 600 ℃.

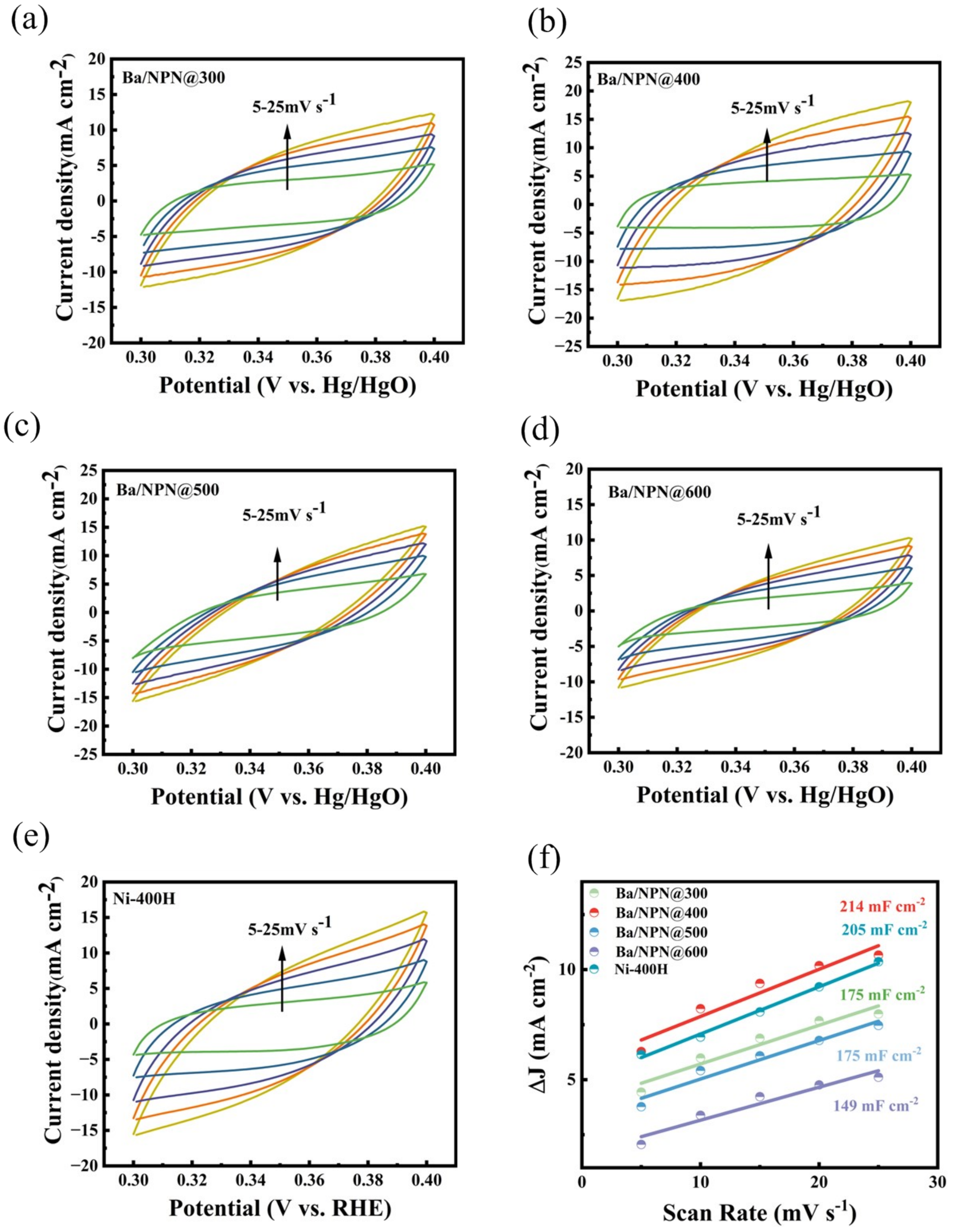

Figure S5. Different current densities versus scan rates for (a) Ba/NPN@300, (b) Ba/NPN@400, (c) Ba/NPN@500, (d) Ba/NPN@600, and (e) Ni-400H. (f) C_{dl} of the Electrodes reduced at different temperatures.

Tabel S1. Comparison of HER performances for Ba/NPN@400 electrode and other electrodes in 1 M KOH at 10 mA cm^{-2}.

Electrodes	η_{10} (mV)	References
Ba/NPN@400	36	This work
NiS–CeO_2	47	*Langmuir*, 2023, **39**, 17929-17938
$NiCo_2O_4/Ni(OH)_2$	84	*International Journal of Hydrogen Energy*, 2021, **46**, 32846-32857
Ni/Co_3O_4	90	*Nano-Micro Letters*, 2022, **14**, 148
Ni/CeO_2	100	*Small*, 2022, **18**, 2106592
CeNiFe-MOF	113	*Chemical Science*, 2025, **16**, 685-692.
4 wt% Ni–Co_3O_4	120	*Journal of Alloys and Compounds*, 2020, **823**, 153750
Sm@NiCu	125	*Acs Applied Energy Materials*, 2023, **6**, 8818-8829

References

1. R. Martínez-Hincapié, J. Wegner, M. U. Anwar, A. Raza-Khan, S. Franzka, S. Kleszczynski and V. Čolić, *Electrochimica Acta*, 2024, **476**, 143663.