

Supplementary Information

Oxygen vacancies confined in nickel oxide nanoprisms arrays for promoted electrocatalytic water splitting

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Experimental section

Preparation of a-NiO nanoprisms arrays on nickel foam

The cleaned Ni foam (2.00*4.00 cm² size) was introduced into a Teflon-lined stainless steel autoclave (with 100 mL space) filled with 60 mL H₂O₂ aqueous solution (30 wt% concentration). The autoclave was then sealed with a lid and maintained at 200 °C for 6 h and subsequently left in an ice-water system to cool rapidly to room temperature within 10 min. Following this, the Ni foam was taken out and rinsed with deionized water several times and then, it was thoroughly. Afterwards, NiO nanoprisms was obtained by annealing at 400 °C in a N₂ atmosphere for 2 h at a heating rate of 10 °C min⁻¹.

Preparation of b-NiO rich in oxygen vacancies and grown on nickel foam

NiO rich in oxygen vacancies (b-NiO) was synthesized via the reduction reaction with NaBH₄ acting as the reductant. Firstly, 0.4 mol NaBH₄ was dissolved in 40 mL deionized water under the help of ultrasonication. Then, a-NiO/NF was inserted in the as prepared NaBH₄ solution under stirring for 5 h at room temperature. The material was also washed with water and ethanol for several times. Finally, the product was dried in vacuum for 5 hours. The b-NiO are obtained.

Characterization of materials

The phase composition and purity of the materials are identified using X-ray powder diffraction (XRD) by Xpert-Pro MPD diffractometer with Cu K α radiation. The morphology of the materials is researched using scanning electron microscopy (SEM) images with Tescan MAIA3 XMH, and the chemical elements of the materials are cataloged using X-ray photoelectron spectra (XPS) tests on PerkinElmer PHI 5000C. The corresponding TEM elemental mapping images were measured using transmission electron microscopy (TEM) with JEOL 2010.

Electrochemical test

Electrocatalytic HER measurements are conducted in a classical three-electrode system controlled by CHI660e electrochemical workstation using graphite (HER) as the counter electrode, Ag/AgCl electrode used as the reference electrode, and the resulting material as the working electrode. The chronopotentiometric measurements was conducted to study their durability for water splitting reaction. The faradic efficiency (FE) was determined as the ratio between the amount of experimental and theoretical hydrogen production.

Faraday efficiency measurement

The same volume of gas sample in the headspace of the electrolytic cell was withdrawn by a SGE gas-tight syringe and analyzed by gas chromatography (GC). The H₂ in the sampled gas was separated by passing through a 2 m \times 3 mm packed

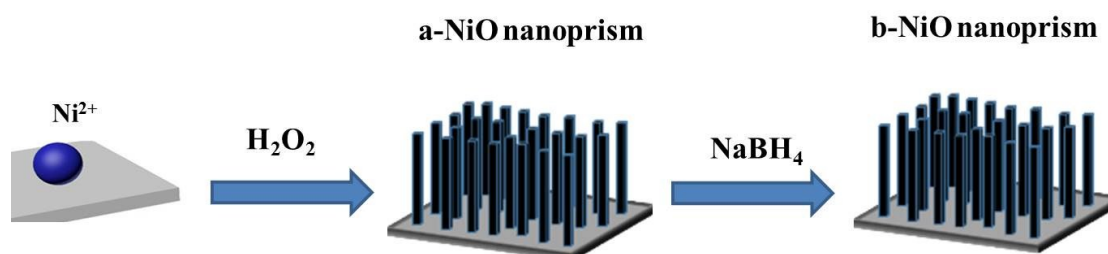
molecular sieve 5A column with an Ar carrier gas and quantified by a Thermal Conductivity Detector (TCD)(Shimadzu GC-9A).

DFT computation details

The DFT calculations were performed using the Cambridge Sequential Total Energy Package (CASTEP) with the plane-wave pseudo-potential method. The geometrical structures of the (001) plane of NiO were optimized by the generalized gradient approximation (GGA) methods. The Revised Perdew-Burke-Ernzerh of (RPBE) functional was used to treat the electron exchange correlation interactions. A Monkhorst Pack grid k-points of $3 \times 3 \times 2$ and a plane-wave basis set cut-off energy of 400 eV were used for integration of the Brillouin zone. The structures were optimized for energy and force convergence set at 0.03 eV/Å and 1.0×10^{-5} eV, respectively. A self-consistence field of 2.0×10^{-6} eV/atom was applied. A vacuum space as large as 15.0 Å was used to avoid periodic interactions.

Table S1. Comparison of water splitting performance for b-NiO/NF with other non-noble-metal water splitting catalysts under alkaline conditions.

Catalyst	Cell voltage	Res.
b-NiO	1.59V	This work
a-NiO	1.70V	This work
Co ₉ S ₈ @NOSC-900	1.60V	[1]
Ni-Fe-MOF	1.55V	[2]
Al-CoP	1.56V	[3]
Co ₃ (PO ₄) ₂	1.48V	[4]
Ni(OH) ₂ @Ni ₃ S ₂	1.57V	[5]
Mo/Mn-Ni _x S _y	1.49V	[6]
Ni ₃ S ₂	1.73V	[7]
M-NiSe	1.50V	[8]
Cu-Co ₉ S ₈	1.49V	[9]



Scheme. S1. Synthetic process of the b-NiO nanoprism.

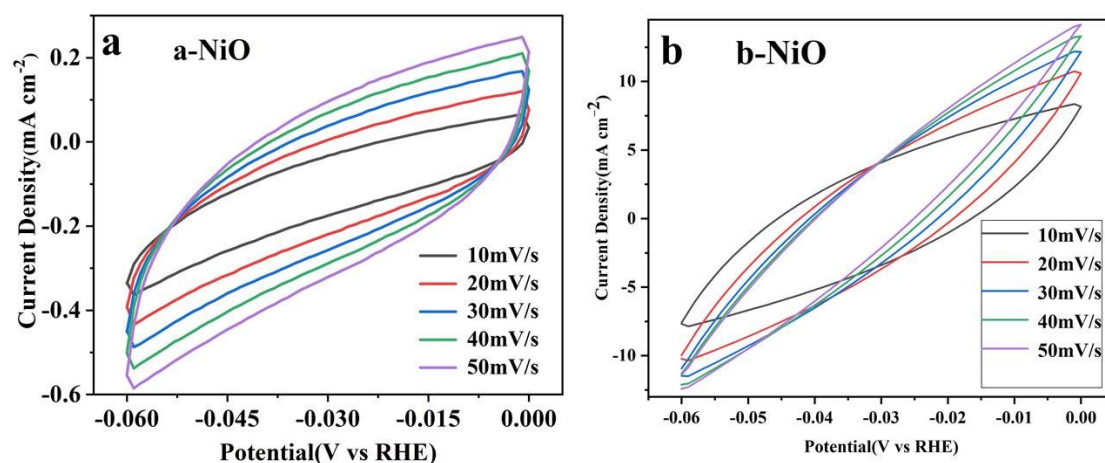


Fig. S1 CV_S of a-NiO (a) and b-NiO (b) with different scan rates (10-50 mV s⁻¹) in the region of -0.06-0.00V vs RHE.

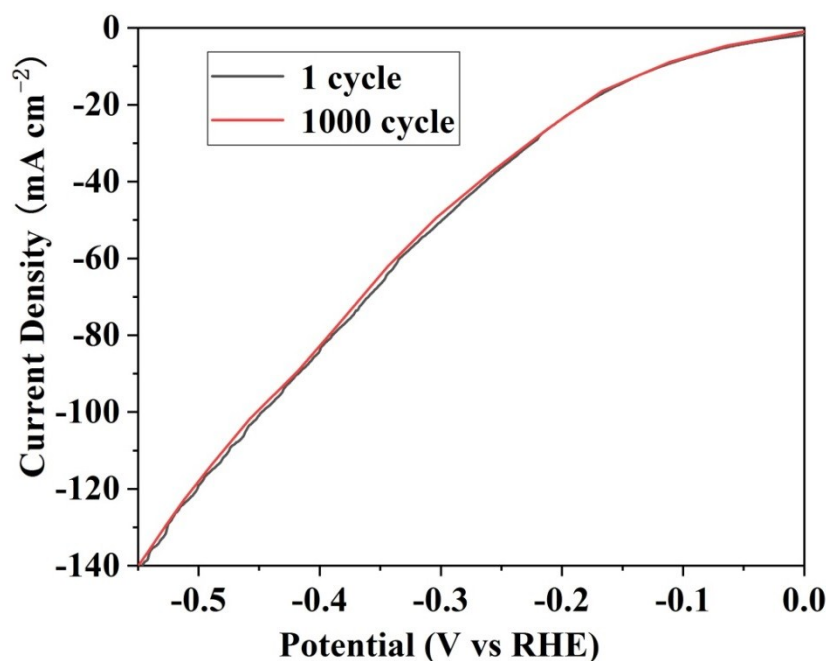


Fig. S2 HER polarization curves for the b-NiO before and after 1000 cycles of the accelerated stability test.

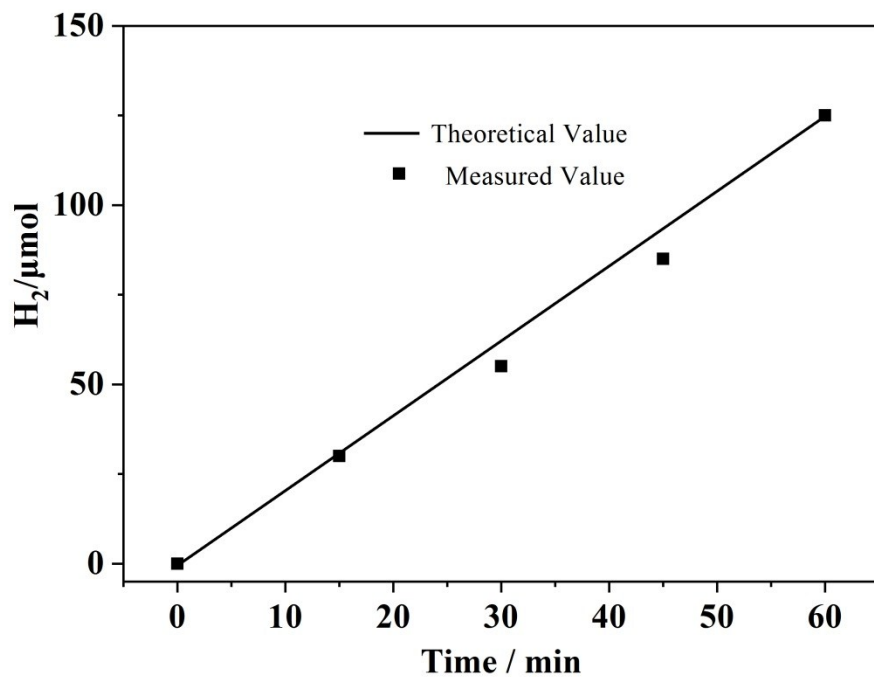


Fig. S3 Electrocatalytic efficiency of H₂ production over b-NiO at a potential of ca. - 0.3 V, measured for 60 min.

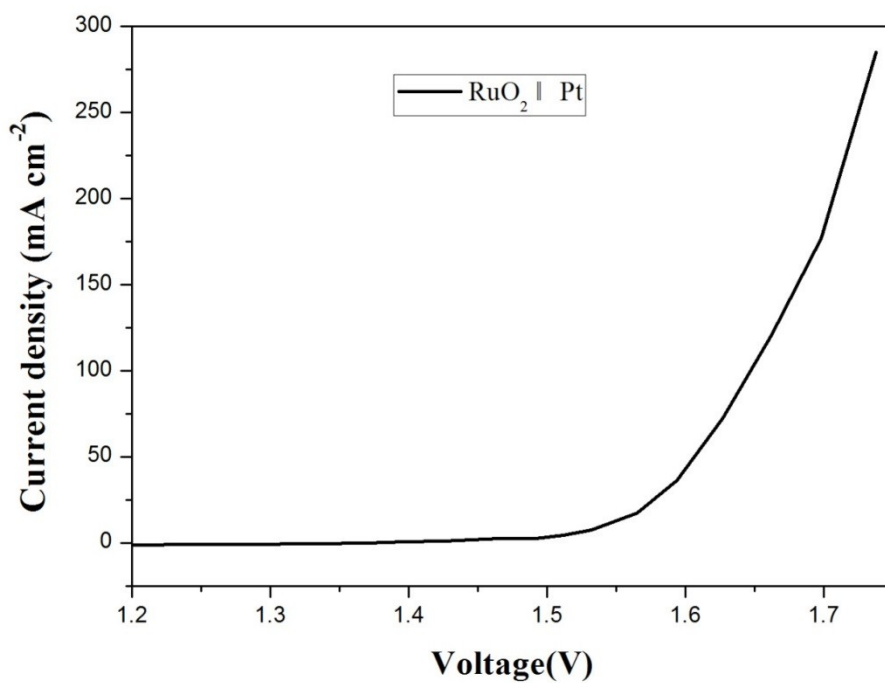


Fig. S4 Polarization curve of the RuO₂ and Pt for water splitting with a scan rate of 5 mV s⁻¹ in 1 M KOH.

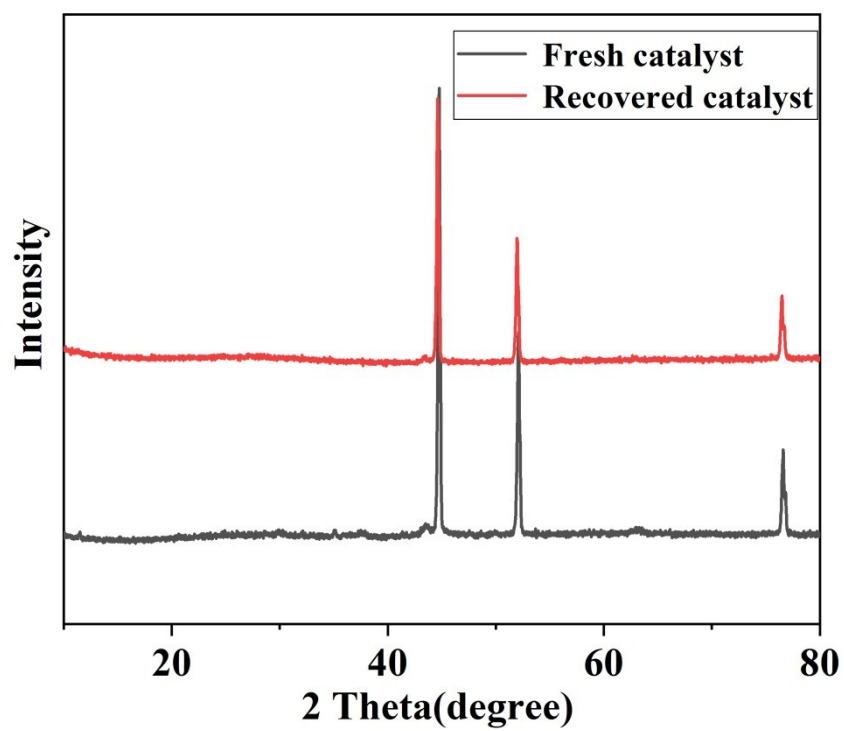


Fig.S5 XRD of fresh and recovered b-NiO.

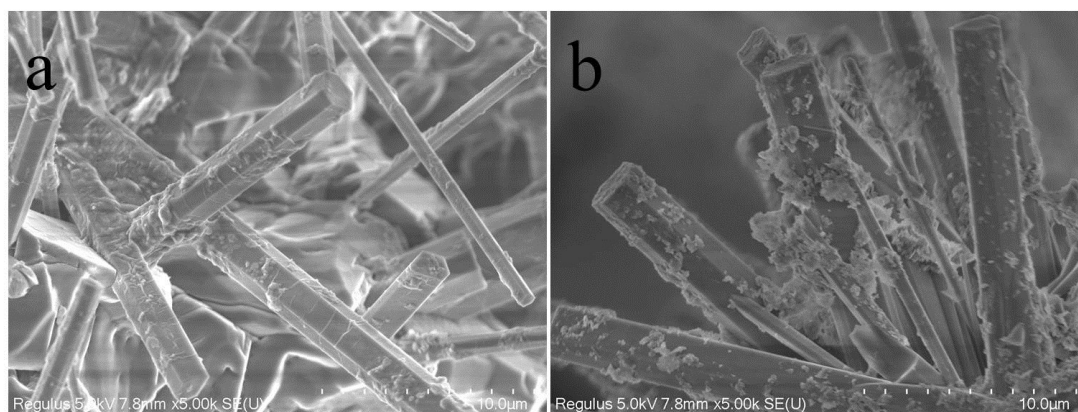


Fig.S6 SEM of fresh (a) and recovered (b) b-NiO.

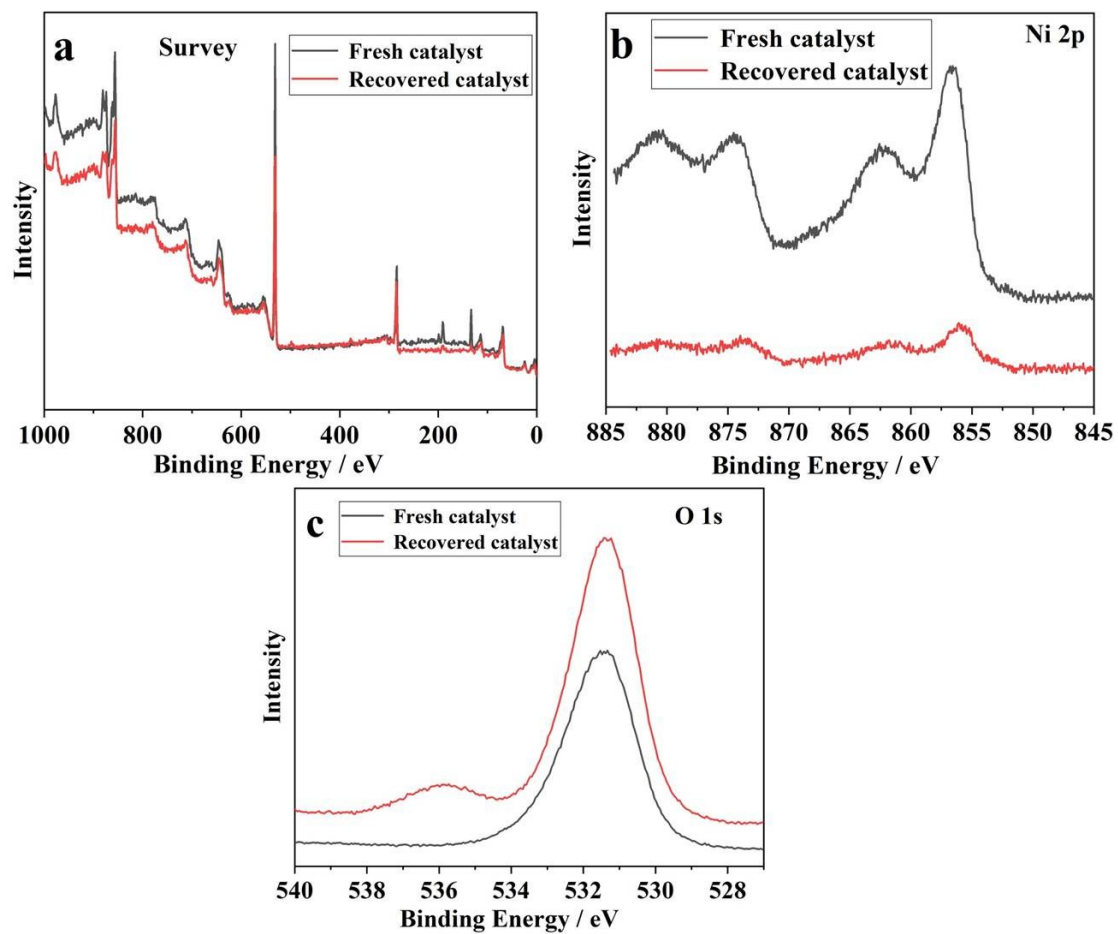


Fig.S7 XPS of (a) survey scan, (b) Ni 2p and (c) O 1s of fresh and recovered b-NiO.

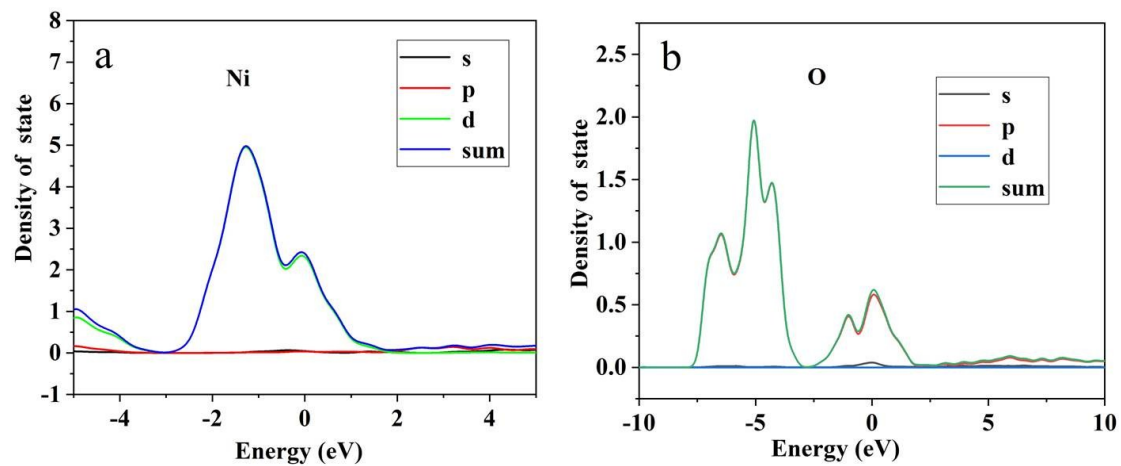


Fig. S8 Calculated density of states for Ni and O in a-NiO.

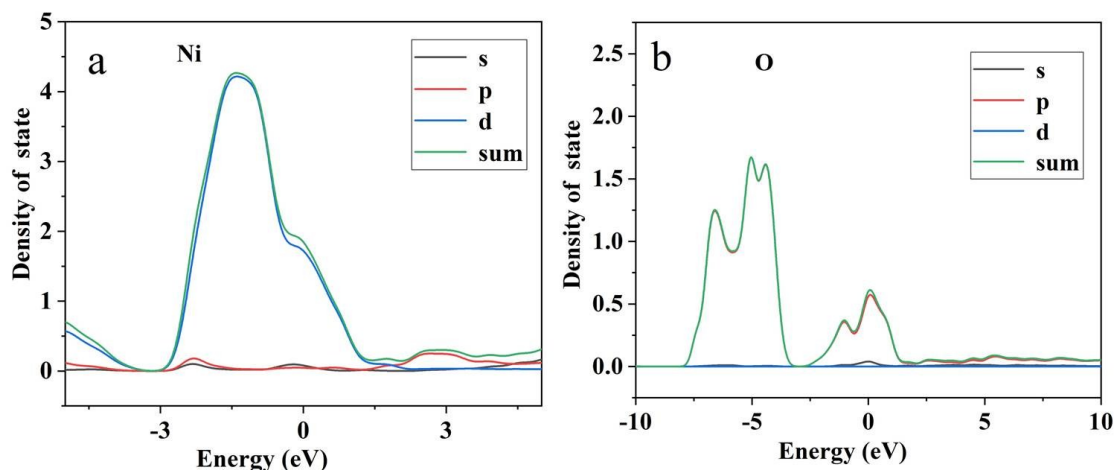


Fig. S9 Calculated density of states for Ni and O in b-NiO.

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