

Supplementary information

of

N⁺ Ions Irradiation Engineering towards Efficient Oxygen Evolution Reaction on NiO Nanosheet Arrays

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2320 kV platform for multi-discipline research with highly charged ions at the
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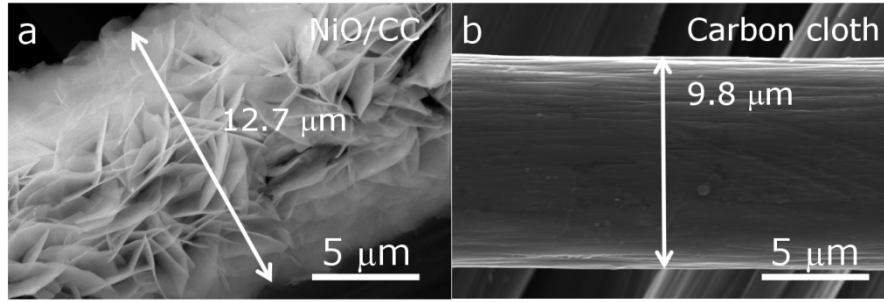


Figure S1 Scanning electron microscope images of bare carbon cloth.

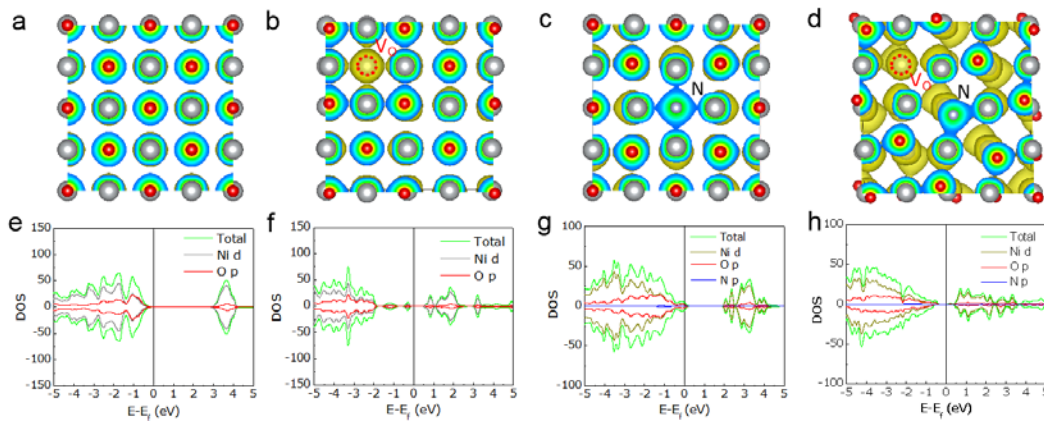


Figure S2 Charge density distribution of (a) NiO, (b) VO introduced NiO, (c) N doped NiO and (d) N, VO coexisted NiO. Calculated DOS results of (a) NiO, (b) VO introduced NiO, (c) N doped NiO and (d) N, VO coexisted NiO.

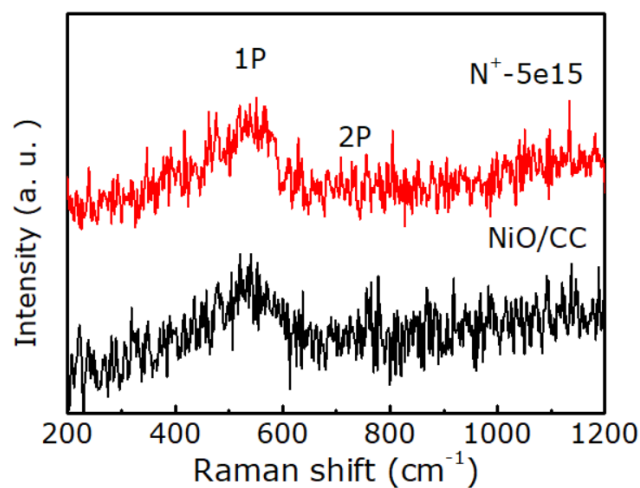


Figure S3 Raman spectra of NiO/CC and N⁺-5e15.

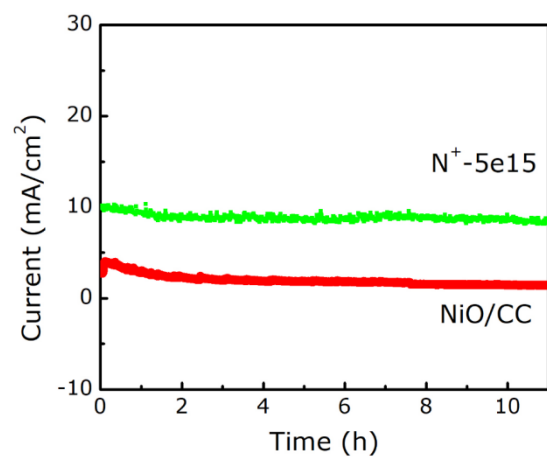


Figure S4 The durability of electrocatalytic electrodes made of NiO/CC and N⁺-5e15.

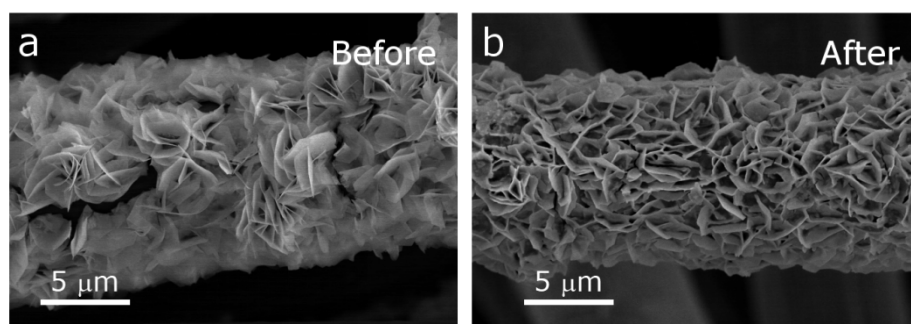


Figure S5 SEM images of N⁺-5e15 captured before and after OER measurement.

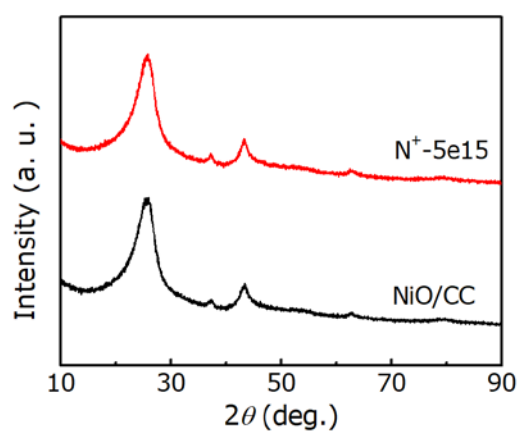


Figure S6 XRD patterns of N⁺-5e15 before and measured after OER cycling.

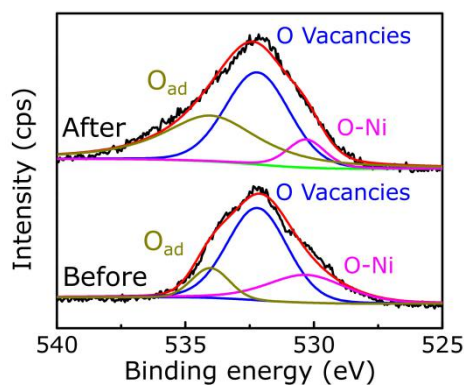


Figure S7 O 1s XPS results of N⁺-5e15 measured before and after OER cycling.

Table S1 OER electrocatalytic performance of several NiO-based electrodes

	η_{10} (V)	η_{100} (V)	Tafel slope (mV/dec)
NiO NSs ^[1]	-	-	225
NiO/Fe ^[2]	1.71	-	-
NiO _x ^[3]	1.92	-	-
FeNC/NiO ^[4]	1.67	-	-
N ⁺ -5e15	1.63	1.98	136

Additional details

Experiments

In this paper, NiO nanosheets loaded on carbon clothes (NiO/CC) were synthesized by hydrothermal and annealing process. Firstly, Ni(NO₃)₂·6H₂O (4.4 mmol, 1.279 g), NH₄F (22 mmol, 0.814 g) and urea (55 mmol, 3.303 g) were dissolved in distilled water (88 mL). After stirring, the solution was transferred to a 100 mL steel autoclave with a piece of carbon cloth (1 cm×3 cm) sealed into the

solution. After heating at 120 °C for 16 h in a vacuum oven, the carbon fiber coated with Ni-LDH was washed with distilled water and ethanol for several times. Subsequently, the as-prepared samples were annealed at 400 °C for 2 h under Ar (50 sccm) atmosphere. After this procedure, the NiO nanosheets loaded on carbon clothes were obtained. Finally, we selected a piece of sample and carried out N⁺ ions irradiation for it. In this experiment, the N⁺ ions were accelerated by a voltage of 50 kV and formed high-energy nitrogen beam, which vertically irradiated on the surfaces of the samples.

Materials Characterizations:

X-ray diffraction spectra (XRD; X'pert Pro Philips with Cu K_α radiation) and were used to study the crystal structure of NiO catalysts. Scanning electron microscopy (SEM; TESCAN MIRA3) and and transmission electron microscopy (TEM; Tecnai G2 F30, FEI) were used to observe the morphology of NiO samples. X-ray photoelectron spectroscopy (XPS; Kratos AXIS UltraDLD), Raman spectra (Jobin-Yvon LabRam HR80, 532 nm) were used to investigate the native vacancies of NiO samples. Electron spin resonance (ESR JEOL, JES-FA300, microwave frequency is 8.984 GHz) measurement was employed to study the resonance field of the samples.

Electrochemical measurement:

The electrochemical measurements were conducted on a CHI 660E electrochemical workstation with a typical three-electrode system. During the measurement, Ag/AgCl electrode was used as the reference electrode, while a Pt filament was employed as the counter electrode. Besides, The sample was held by conductive clamp, was regarded as the working electrode. All the OER tests were carried out in 0.1 M KOH electrolyte (pH=13). Before the measurement, it takes 8000-10000 cycles of CV measurement (in the range of 0-0.2 V) to active the electrodes to the stable status. Linear sweep voltammetry (LSV) was measured with a scan rate of 2 mV/s. In this experiment, the practical overpotentials were calibrated with respect to a reversible hydrogen electrode using $E_{RHE} = E_{Ag/AgCl} + 0.059 \times 13$ mV. The cyclic voltammetry (CV) measurement was conducted with the range from 0 V to 0.2 V by different scan rates (from 20 mV/s to 180 mV/s). Electrochemical impedance spectroscopy (EIS) measurements were carried out with frequencies ranging from 0.1 Hz to 100 kHz at the voltage of -500 mV (vs. RHE). A simplified Randles circuit was used to fit the impedance data to extract the solution (R_s) and charge-transfer resistance (R_{ct}). The turnover frequency (TOF) was calculated with the equation: $TOF = I/Q$, where I (A) obtained from the LSV measurements is the current of the polarization curve. Voltammetry charges (Q) is calculated by the following equation: $Q = 2Fn$, Where F is Faraday constant (96480 C/mol), n is the number of active sites. In the experiment, the voltammetry curve is obtained by CVs measurements with phosphate buffer solution (pH = 7) at the scan rate of 50 mV/s. The number of Q is evaluated after deducting the blank value. The derivation and calculation follow the

equations: $Q=CU=iU/v$. In a CV curve, i and U are changing, so we can get by integral the CV curve, where v is the scan rate (50 mV/s). In the experiment, the relationship between impedance (Z) and voltage is established for both NiO/CC and N^+-5e15 electrodes. The capacitance (C) is calculated using the equation: $C = -1/2 \pi f Z$, where f is the fixed frequency of voltage, which is set as 100 Hz during the measurement and Z is the impedance.

First-principle calculations:

Our first-principles calculations were carried out by Vienna ab initio simulation package (VASP) based on density functional theory (DFT).^[5] Projector augmented wave (PAW) potentials was utilized to simulate electron-ion interactions.^[6] In addition, the generalized gradient approximation with Perdew Burke Ernzerhof (GGA-PBE) functional were employed to approximate exchange and correlation effects when relaxing the atomic structure, where all models were fully relaxed with self-consistency accuracy of 10^{-5} eV.^[7] The cut-off energy (450 eV) for the plane-wave basis restriction and the K -points were taken under Monkhorst-Pack for the Brillouin-zone integration. To prevent interaction between two neighboring surfaces, a vacuum slab of 20 Å was employed in z direction for NiO with the calculated fully relaxed lattice constants of $a = b = c = 4.18$ Å. A 2×2 supercell was used to calculate the electronic property and hydrogen evolution activity.

References

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