

## Supporting Information

### ***In situ* grown hierarchical NiO nanosheet@nanowire arrays for a high-performance electrochromic energy storage application**

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### **Experimental section**

#### **Materials**

Nickel nitrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), urea ( $\text{CH}_4\text{N}_2\text{O}$ ), nickel(II) acetate tetrahydrate ( $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ ), ethanol ( $\text{C}_2\text{H}_6\text{O}$ ), and KOH were used directly without any further purification.

#### **Pre-seed layer treatment**

FTO coated glass substrates ( $30 \times 50 \text{ mm}^2$  in size) were carefully ultrasonicated in acetone, ethanol and DI water sequentially for 0.5 h to obtain clean surface. Subsequently, the FTO glass substrates were immersed in a 15 mM  $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  at  $65^\circ\text{C}$  for 0.5 h. Then, the treated glass was transferred to heating plate and annealed at  $275^\circ\text{C}$  for 0.5 h in air.

#### **Synthesis of hierarchical NiO nanosheet@nanowire arrays**

The hierarchical NiO arrays were synthesized by one-step hydrothermal process following heat treatment procedure. First, 290 mg  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and 600 mg  $\text{CH}_4\text{N}_2\text{O}$  were transferred in 40 mL DI water and 10 mL ethanol and stirred until the solution became clear. The mixed solution was subsequently poured into a 100 mL autoclave, and the post-treated FTO glass substrates were immersed in the solution to

initiate growth of the film. NiO precursor layer was obtained by solution phase reaction at 120°C for 1, 3, 6 and 9 h. When the autoclave was cooled down naturally, the obtained precursor films were carefully cleaned with flowing deionized water and ethanol for 5 minutes, respectively. Subsequently, this precursor was then transformed into NiO by heat treatment at 350°C for 2 h in air with a heating rate of 2 °C/min. The synthesized NiO films are named as NiO-X, where X stands for the different hydrothermal time. A schematic illustrating the experiment procedure is given in Scheme 1.

### **Material Characterization**

The micro size and morphology feature of the synthesized samples were analyzed by using SEM (Hitachi Regulus 8230) and TEM (JEM-2100F). XRD patterns of the samples from 10 to 90 degrees were examined on a X'Pert Pro MPD (PANalytical B.V.) with Cu K $\alpha$  radiation ( $\lambda= 1.54 \text{ \AA}$ ). XPS data was examined with A Thermo ESCALAB250Xi system using Al K $\alpha$  radiation.

### **Electrochemical tests**

Electrochemical tests were performed with a three-electrode system. 1 M KOH aqueous solution was used as the reaction electrolyte. The synthesized NiO sample, an Ag/AgCl electrode and a clean Pt wire electrode were used as the working, reference and counter electrode, respectively. Chronoamperometry (CA), cyclic voltammetry (CV), i-t curve and galvanostatic charge–discharge (GCD) measurements were tested accompanying corresponding *in situ* spectroscopic test at 550 nm by an electrochemical workstation (CHI760E) and a Shimadzu UV-3600 UV-VIS-NIR spectrophotometer. Detailly, the CV measurements were tested in the applied voltage

range of -1.0~1.0 V with scan rate of 0.005 V/s. The optical transmittance of the film was tested over the wavelength range from 300 to 1300 nm. The dynamic optical modulation was obtained at 550 nm by applying voltage between -1.0 V and 1.0 V with a duration of 20 s for each step. Electrochemical impedance spectroscopy (EIS) was tested with AC amplitude of 0.005 V with a frequency range of 0.1~100 kHz. The calculated mass loading of the NiO-3h electrode is 0.037 mg cm<sup>-2</sup>.

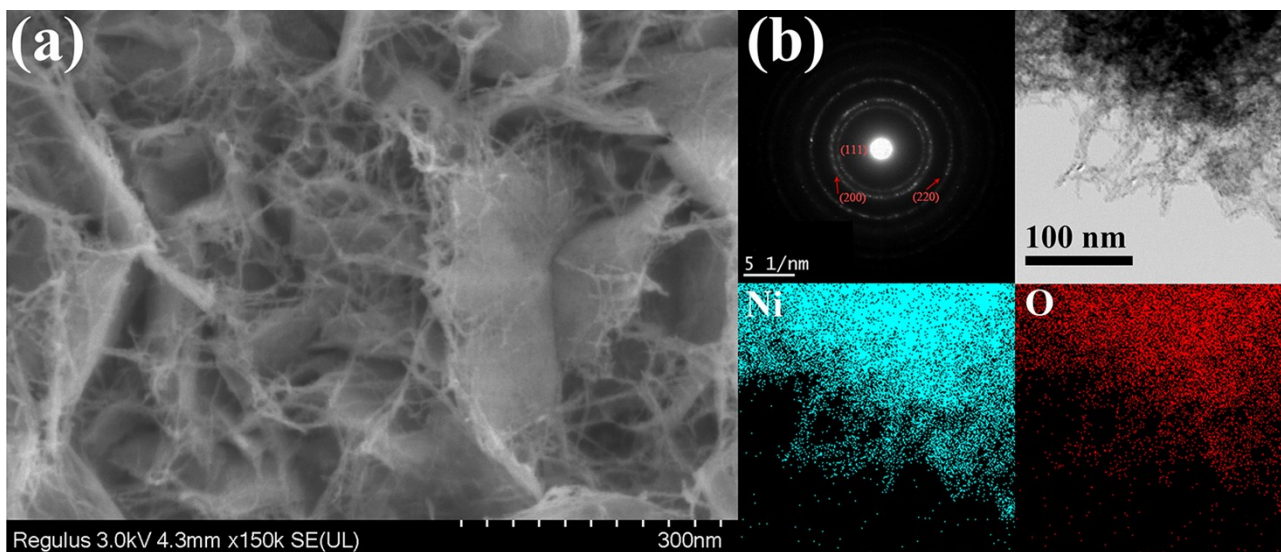


Figure S1. (a) High magnification FESEM image and (b) corresponding SAED patterns and EDS maps of NiO-3h.

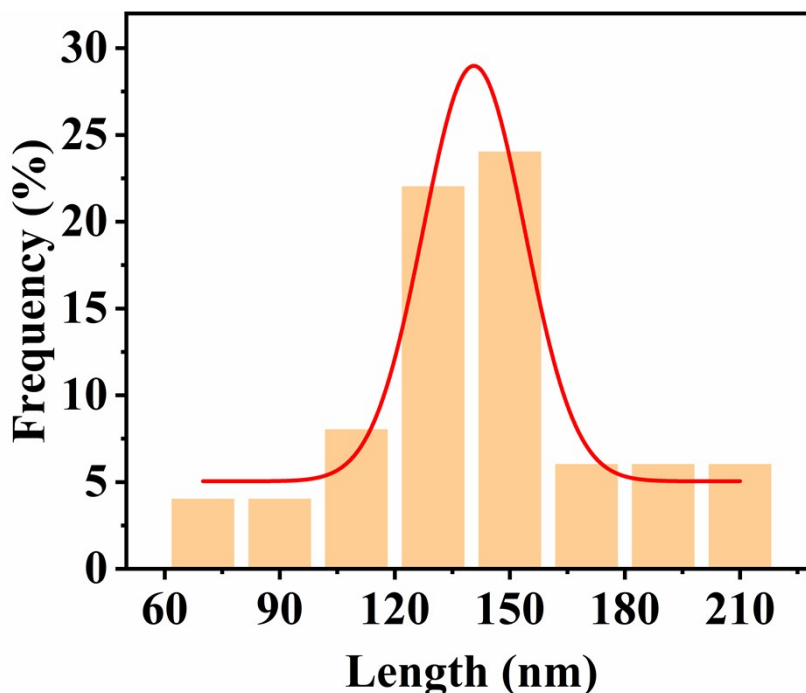


Figure S2. Statistical analysis of the length of NiO-3h.

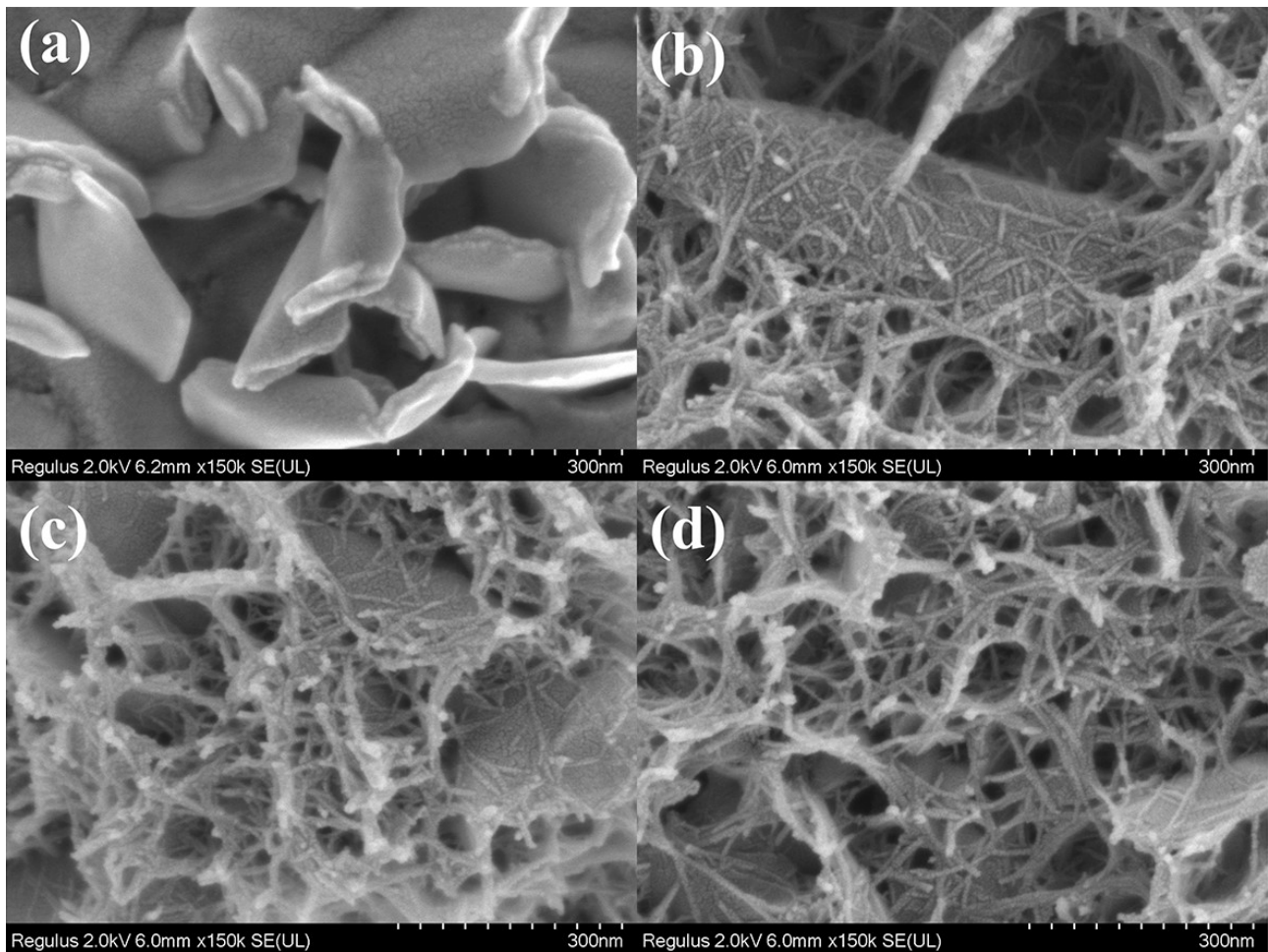


Figure S3. FESEM image of the precursors of (a) NiO-1h, (b) NiO-3h, (c) NiO-6h and (d) NiO-9h.

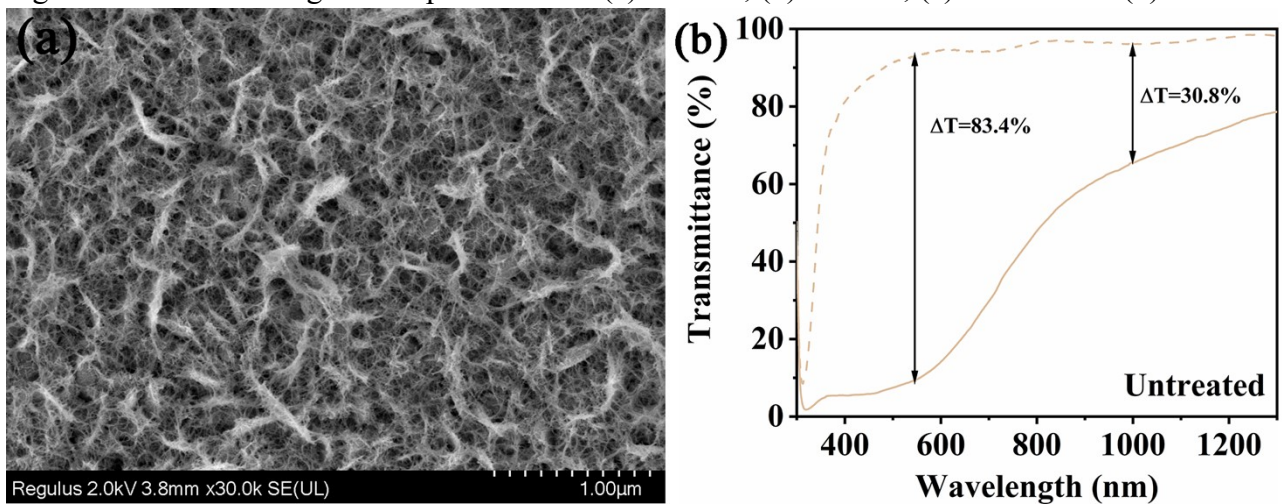


Figure S4. (a) FESEM image and (b) transmittance spectra of NiO-3h synthesized under the same conditions but without the seed layer treatment of the FTO substrate.

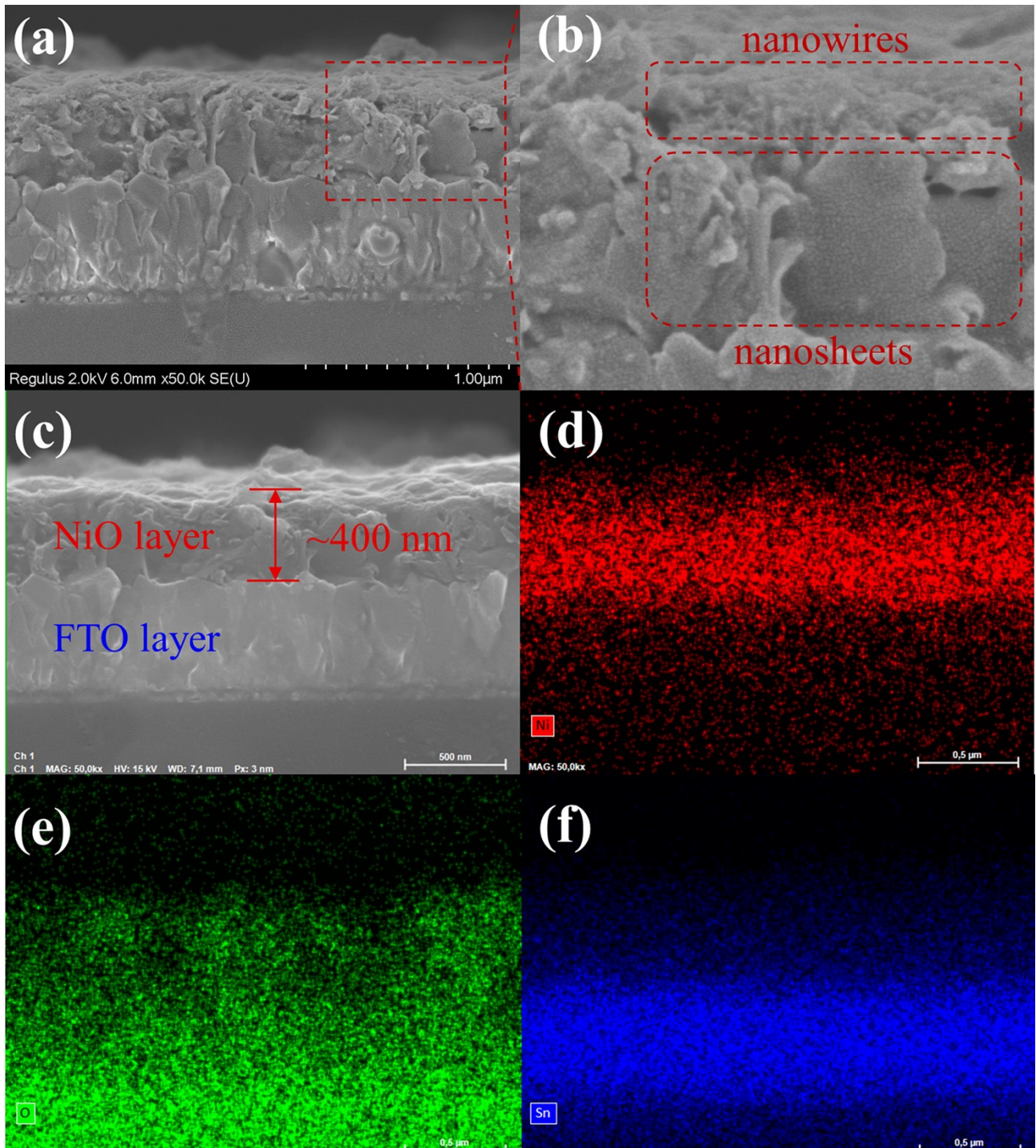


Figure S5. The FESEM picture of cross-sectional view and corresponding EDS maps of NiO-9h.

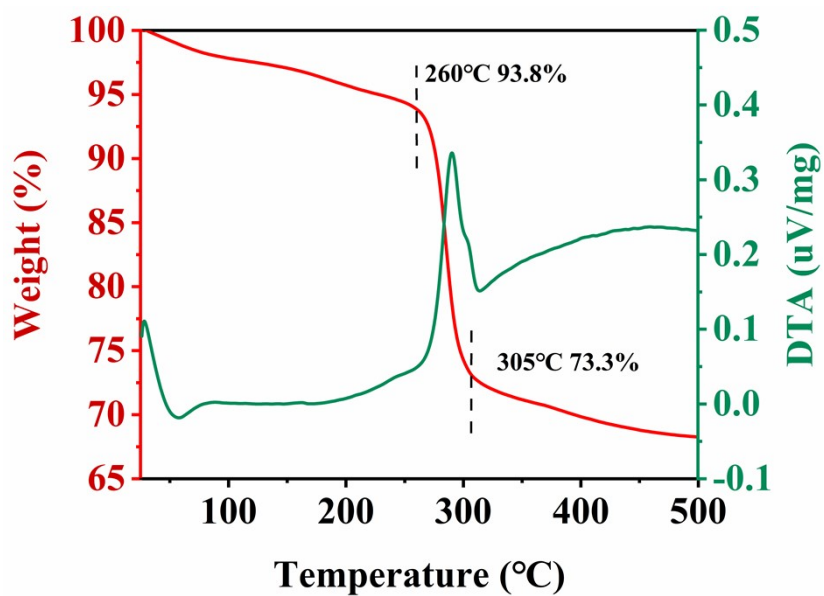


Figure S6. TGA and DTA curves of the NiO precursor.

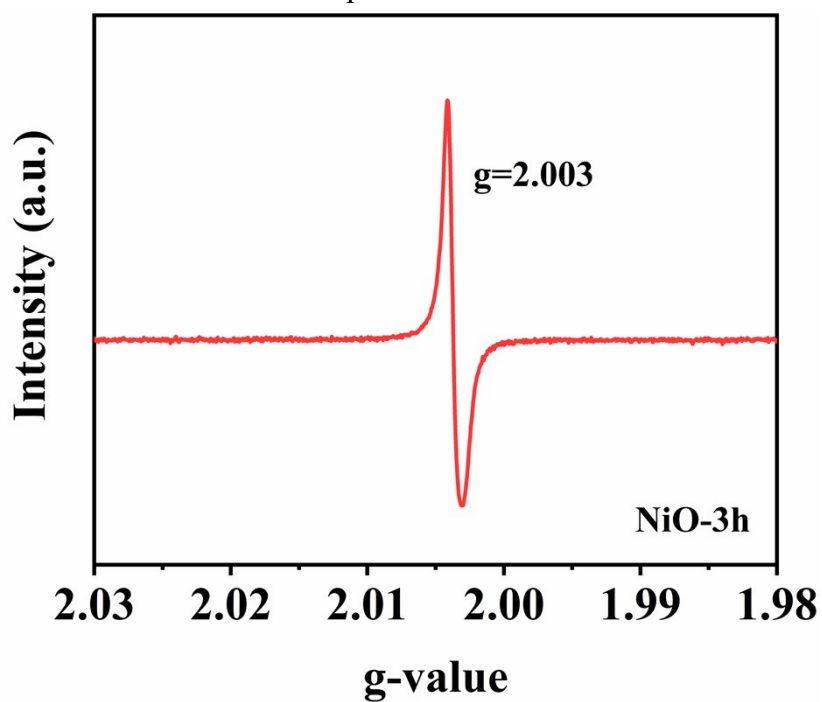


Figure S7. EPR spectrum of the NiO-3h film.

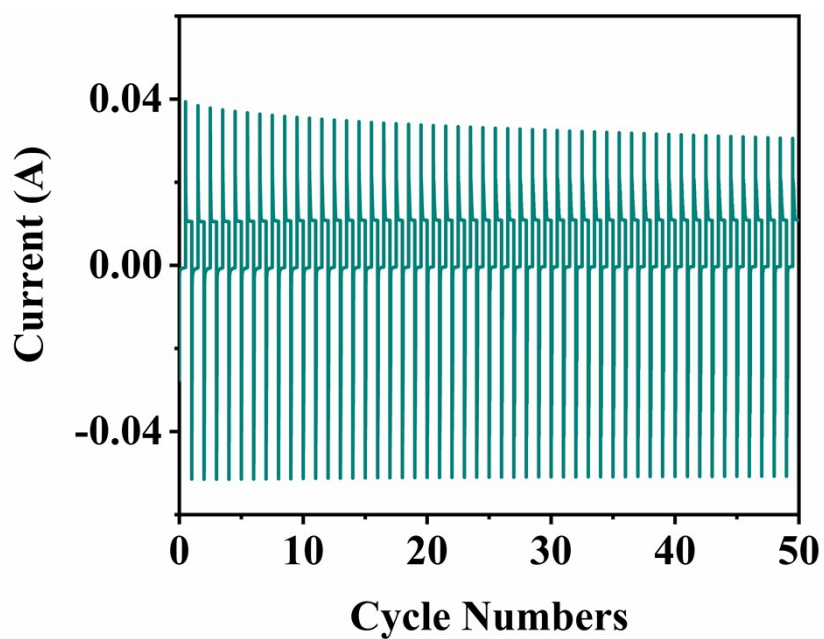


Figure S8. Current profile of the NiO-3h with a square wave potential oscillating between +1.0 and -1.0 V in an activation process.

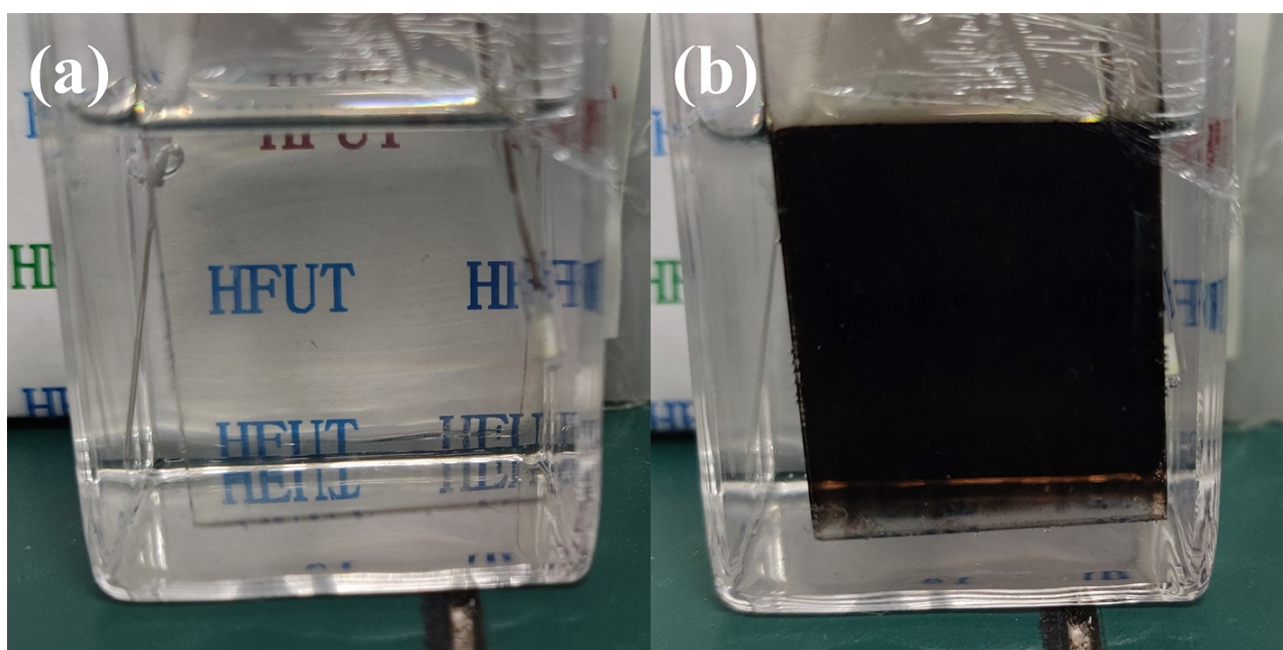


Figure S9. Optical photographs of NiO-3h at (a) bleached state and (b) colored state.

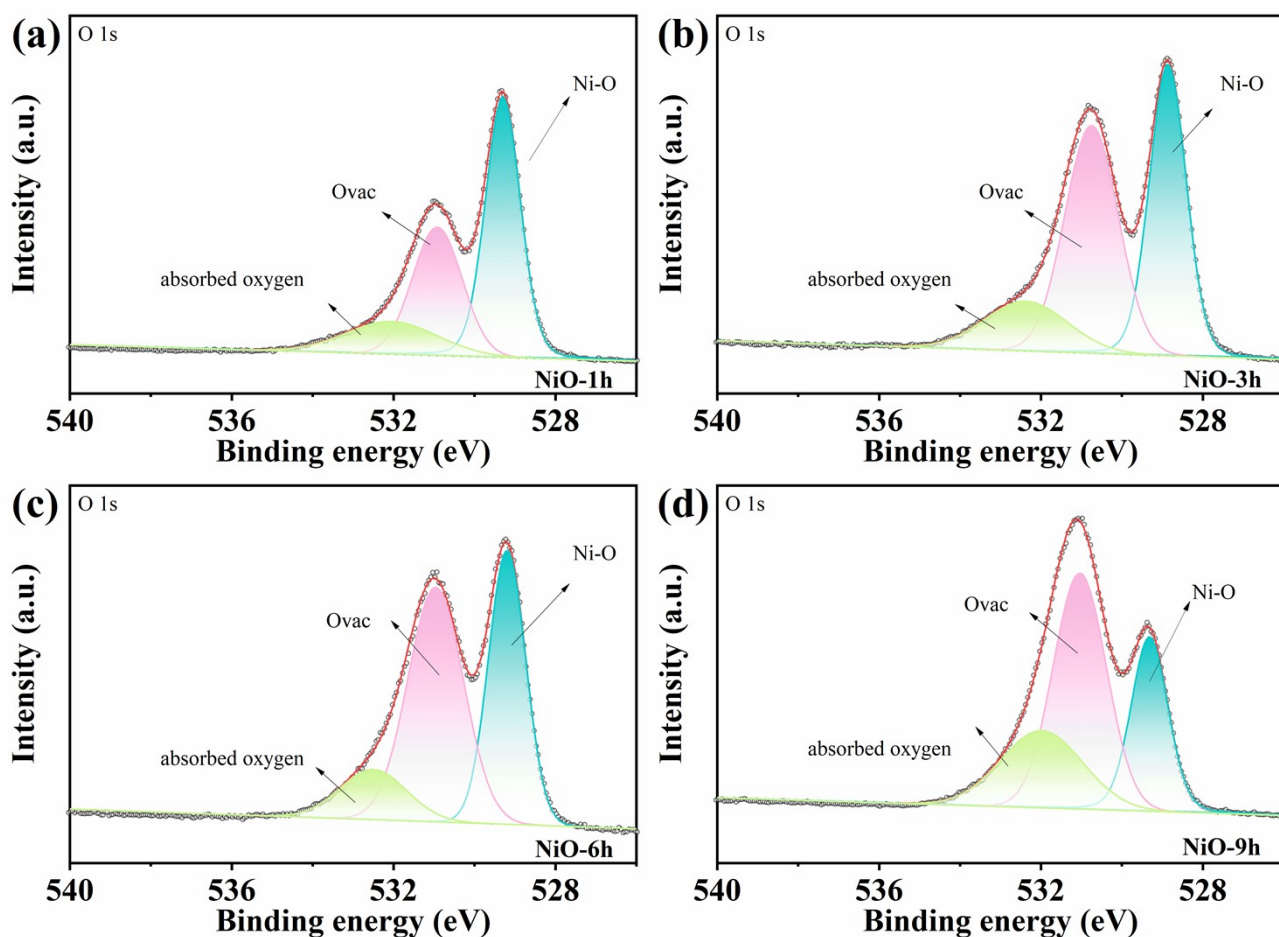


Figure S10. XPS O 1s spectrum of (a) NiO-1h, (b) NiO-3h, (c) NiO-6h and (d) NiO-9h.

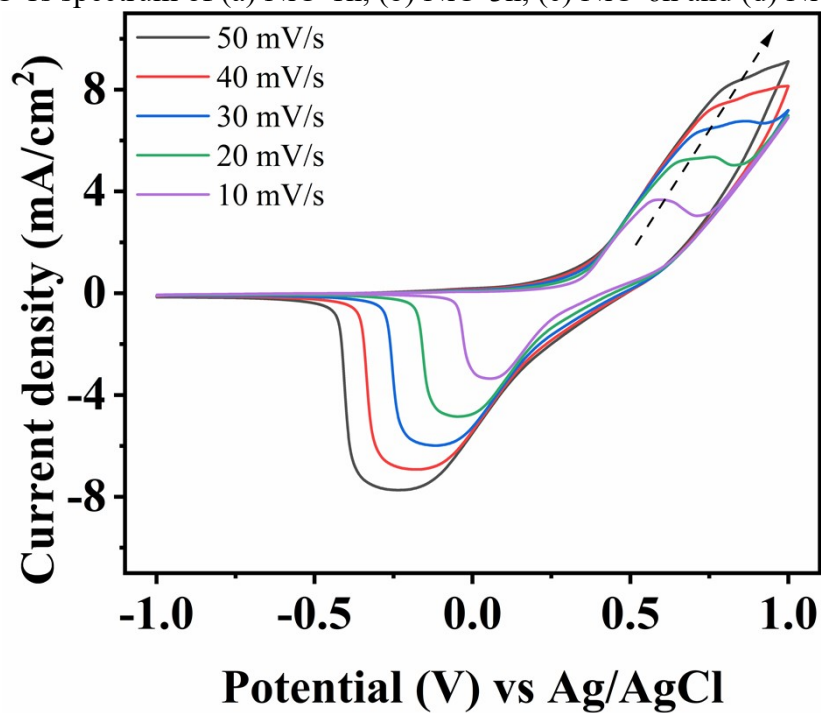


Figure S11. CV curves of NiO-3h at various scan rates.



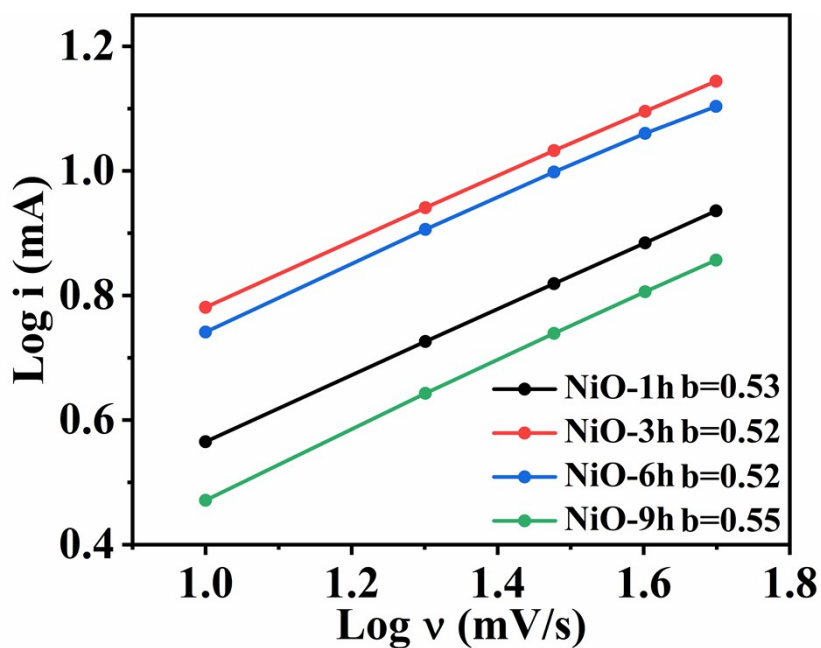


Figure S12. The power law relationship between the peak currents and scan rates of the NiO-3h thin films.

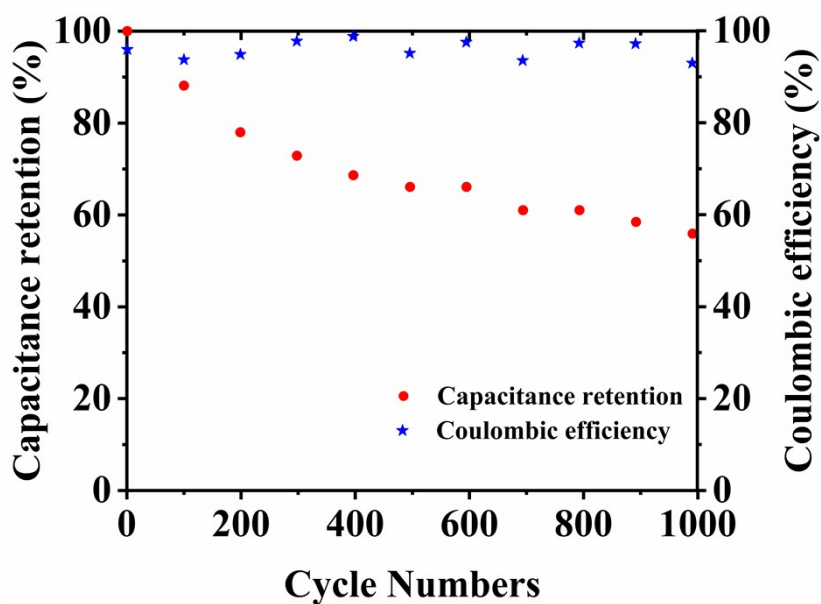


Figure S13. Capacitance retention and coulombic efficiency of the NiO-3h electrode over 1000 cycles at a current density of  $0.42 \text{ mA/cm}^2$ .

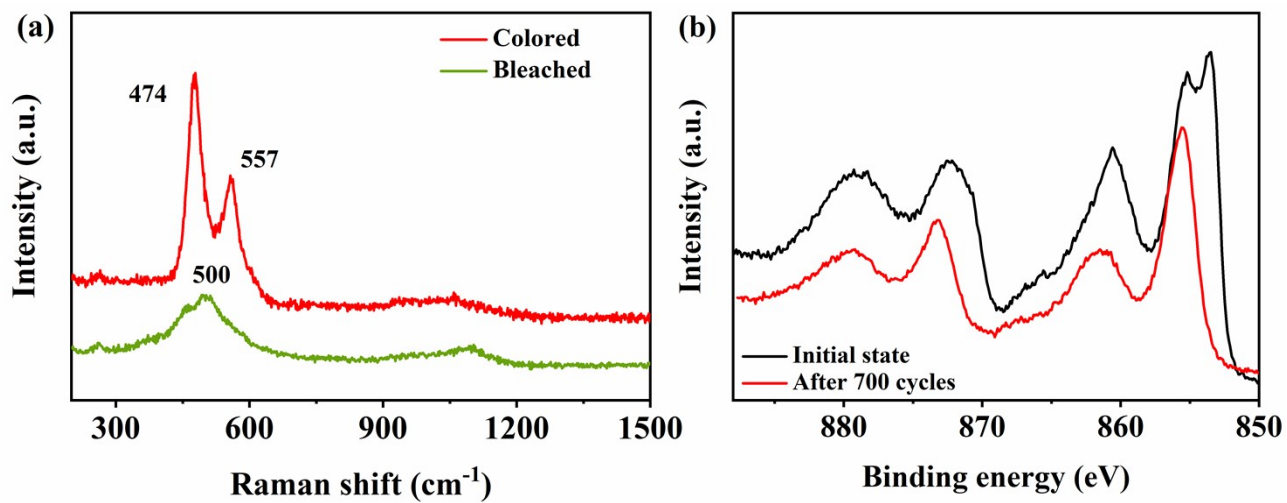


Figure S14 (a) Raman spectra of the coloring and bleaching states of NiO-3h film after 700 cycles. (b) Ni 2p of NiO-3h at different cycling times.

Film	Coloring Time (s)	Bleaching Time (s)
NiO-1h	6	2.2
NiO-3h	9.8	5.4
NiO-6h	5.6	3.2
NiO-9h	5.8	3.2

Table S1. Switching time of the NiO samples.

Sample	$\Delta T$	CE ( $\text{cm}^2\text{C}^{-1}$ )	Cycle stability	Capacitive performance	References
NiO	63.6% at 550 nm	42.8	90.8% after 3000C	308 F/g at 2 A/g	7
Al-doped NiO	58.4% at 500 nm	54.2	30% decrease after 2000C	NA	11
NiO-Co5	52% at 550 nm	NA	NA	88.24 $\text{mF}/\text{cm}^2$ at 0.4 $\text{mA}/\text{cm}^2$	40
NiO	51% at 550 nm	40	<10% after 3000C	NA	41
N-doped carbon coated NiO	54.27% at 450 nm	48.5	NA	235.8 F/g at 2 A/g	42
Li-doped NiO	66.8% at 550 nm	31.2	NA	13 $\text{mF}/\text{cm}^2$ at 0.1 $\text{mA}/\text{cm}^2$	43
NiO nano-sheets	66.9% at 550 nm	48.51	NA	129.32 $\text{mF}/\text{cm}^2$ at 5 $\text{mV}/\text{s}$	44
NiO MS-HMS	47% at 600 nm	85.3	NA	NA	45
Hierarchical NiO film	95% at 550 nm	91.2	86.5% after 700C	117.2 $\text{mF}/\text{cm}^2$ at 0.14 $\text{mA}/\text{cm}^2$	This work

Table S2. A summary of electrochromic energy storage performance based on different nickel oxide materials.