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 (Ni(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O), urea (CH\textsubscript{4}N\textsubscript{2}O), nickel(II) acetate tetrahydrate (Ni(CH\textsubscript{3}COO)\textsubscript{2}·4H\textsubscript{2}O), ethanol (C\textsubscript{2}H\textsubscript{6}O), and KOH were used directly without any further purification.

**Pre-seed layer treatment**

FTO coated glass substrates (30×50 mm\textsuperscript{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 Ni(CH\textsubscript{3}COO)\textsubscript{2}·4H\textsubscript{2}O at 65°C for 0.5 h. Then, the treated glass was transferred to heating plate and annealed at 275°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 Ni(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O and 600 mg CH\textsubscript{4}N\textsubscript{2}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 Kα radiation (λ= 1.54 Å). XPS data was examined with A Thermo ESCALAB250Xi system using Al Kα 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\(^{-2}\).

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 mA/cm².
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.
| Sample                        | ΔT (%) at 550 nm | CE (cm²C⁻¹) | Cycle stability          | Capacitive performance | References |
|-------------------------------|------------------|-------------|--------------------------|------------------------|------------|
| NiO                           | 63.6%            | 42.8        | 90.8% after 3000C        | 308 F/g at 2 A/g       | 7          |
| Al-doped NiO                  | 58.4%            | 54.2        | 30% decrease after 2000C | NA                     | 11         |
| NiO-Co5                       | 52%              | NA          | NA                       | 88.24 mF/cm² at 0.4 mA/cm² | 40         |
| NiO                           | 51%              | 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%            | 31.2        | NA                       | 13 mF/cm² at 0.1 mA/cm² | 43         |
| NiO nano-sheets               | 66.9%            | 48.51       | NA                       | 129.32 mF/cm² at 5 mV/s | 44         |
| NiO MS-HMS                    | 47%              | 85.3        | NA                       | NA                     | 45         |
| Hierarchical NiO film         | 95%              | 91.2        | 86.5% after 700C         | 117.2 mF/cm² at 0.14 mA/cm² | This work  |

Table S1. Switching time of the NiO samples.

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