

Article

Towards Solution-Derived Electrochromic Nickel(II) Oxide Thin Films

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Abstract

The properties of solution-derived nickel oxide (NiO) thin films are strongly influenced by precursor chemistry and post-deposition thermal treatment. In this work, NiO thin films were deposited on indium tin oxide (ITO)-coated glass substrates by chemical solution deposition using a spin-coating process. A 0.6 M nickel acetylacetonate-derived precursor solution prepared in a methanol–propionic acid solvent system was used as the starting solution. The films were thermally treated at 600 °C under continuous oxygen flow, with annealing holding times of 2, 4, and 6 h, to evaluate the effect of thermal-treatment duration on phase formation, surface morphology, and electrochemical redox behavior. Thermal and infrared analyses confirmed precursor decomposition and the formation of nickel–oxygen bonding after thermal conversion. X-ray diffraction confirmed the formation of single-phase cubic NiO at all holding times, while quantitative peak analysis indicated a modest increase in crystallite size from 12.4 to 13.9 nm with prolonged annealing. Atomic force microscopy revealed continuous and homogeneous film surfaces, with low root-mean-square roughness values in the range of 2.5–2.7 nm. Cyclic voltammetry in a LiClO₄/propylene carbonate electrolyte showed a reversible redox response associated with the Ni²⁺/Ni³⁺ transition, accompanied by visible switching between bleached and colored states. The results indicate that annealing holding time affects the structural and morphological characteristics of spin-coated NiO thin films, while the electrochemical measurements confirm reversible redox activity in the investigated sample. These findings provide a processing-oriented basis for evaluating thermal-treatment conditions in solution-derived NiO films intended for electrochemical and optical modulation applications.



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1. Introduction

Nickel oxide (NiO) is a p-type transition-metal oxide widely studied as an anodic electrochromic material because of its chemical stability, low cost, and reversible nickel-ion redox activity involving nickel species [1,2]. The electrochemical response of NiO is commonly associated with the Ni²⁺/Ni³⁺ redox couple, which can produce visible switching

between bleached and colored oxidized state [3–5]. However, the reversibility and intensity of this response are strongly influenced by the structural and morphological characteristics of the film, including phase purity, crystallinity, surface roughness, film continuity, residual precursor-derived compounds, and adhesion to the transparent conducting substrate [6–11]. Several methods have been used to prepare NiO-based thin films, including magnetron sputtering, chemical solution deposition, spin coating, spray pyrolysis, chemical bath deposition, electrodeposition, and aerosol-assisted chemical vapor deposition [1,2,8,12–18]. These routes differ in processing complexity, film density, surface morphology, thickness control, porosity, and compatibility with transparent conducting substrates. A concise comparison of selected preparation methods is given in Table 1. Among these methods, chemical solution deposition combined with spin coating is attractive because it allows NiO films to be obtained from chemically designed precursor solutions by a simple and scalable process [8,10,13]. Nevertheless, solution-derived NiO films are particularly sensitive to precursor chemistry, solvent composition, drying, thermal decomposition, annealing atmosphere, and annealing duration. These parameters control oxide formation, crystallinity, surface morphology, and the accessibility of electrochemically active sites [8–11,13,14].

Table 1. Comparison of selected preparation methods for NiO-based electrochromic thin films.

Method	Main Processing Variables	Typical Advantages	Relevance to This Work
Magnetron sputtering	Sputtering power, oxygen partial pressure, film thickness	Dense, uniform films with good adhesion and controlled thickness	Useful benchmark for high-quality NiO films, but requires vacuum processing [6,12,19]
Aerosol-assisted CVD	Precursor transport, deposition time, substrate temperature	Enables electrochromic and colorimetric evaluation of NiO films	Demonstrates the need for quantitative optical/electrochromic metrics [20]
Chemical solution deposition/spin coating	Precursor chemistry, solvent composition, coating cycles, drying and annealing conditions	Simple, low-cost, scalable, and compatible with ITO/glass substrates	Central method of the present work; film quality depends strongly on precursor conversion and thermal treatment [8,10,13,21]
Spray pyrolysis	Substrate temperature, solvent type, droplet size, spray rate	Suitable for large-area solution-based oxide films	Shows the sensitivity of NiO film properties to solvent and thermal processing [14]
Chemical bath deposition	Bath composition, pH, deposition time, post-annealing	Can produce porous films with improved electrolyte accessibility	Highlights the role of porosity and electrolyte access in NiO electrochemical response [15,16]
Electrodeposition	Applied potential/current, electrolyte composition, deposition time	Direct formation on conductive substrates at relatively low temperature	Provides electroactive films whose thickness and porosity depend on electrochemical parameters [17]

Previous investigations have shown that deposition and post-treatment conditions can substantially modify the growth, morphology, optical response, and electrochemical behavior of NiO-based films. Sialvi et al. investigated the electrochromic and colorimetric properties of NiO films prepared by aerosol-assisted chemical vapor deposition [20,22]. Xie et al. related improved electrochromic behavior to the nanocrystalline structure of NiO electrodes [23], while Guillemot et al. demonstrated that UV treatment and annealing temperature influence the growth and properties of solution-processed NiO films [21]. Thickness-dependent oxidation has also been shown to affect the structural and optical response of sputtered Ni/NiO ultrathin films [22].

Despite previous studies on the electrochromic and colorimetric behavior of aerosol-assisted chemical vapor-deposited NiO films [20], thickness-dependent oxidation in sputtered Ni/NiO ultrathin films [22], nanocrystal-controlled electrochromic performance [23], and post-treatment effects in solution-processed NiO films [21], a specific research gap remains regarding the influence of annealing holding time at a fixed temperature. In particular, its effect on precursor conversion, NiO phase formation, surface morphology, and electrochemical redox behavior has not been systematically evaluated for spin-coated NiO films prepared from a nickel acetylacetonate-derived precursor in a methanol–propionic acid solvent system. It therefore remains unclear whether prolonged annealing promotes further precursor conversion and structural ordering or produces only limited changes in morphology and $\text{Ni}^{2+}/\text{Ni}^{3+}$ redox activity.

Thus, this study aims to assess the influence of annealing holding time on precursor conversion, NiO phase formation, surface morphology, and electrochemical redox behavior in solution-derived NiO thin films. We hypothesize that extending the holding time modifies the films' crystallinity and surface morphology, which may in turn alters the reversible $\text{Ni}^{2+}/\text{Ni}^{3+}$ redox process and the resulting electrochemical response. To test this, NiO thin films were spin-coated onto indium tin oxide (ITO) coated glass substrates using a 0.6 M nickel acetylacetonate-derived precursor solution prepared in a methanol–propionic acid solvent system. The films were then annealed at 600 °C under a continuous oxygen flow for 2, 4, and 6 h, while all other processing variables kept constant. To map processing–structure–morphology–property correlations, the films were characterized using thermal and infrared analyses, XRD, AFM, cyclic voltammetry, and qualitative visible color switching. This work focuses on these material correlations rather than a comprehensive device-level electrochromic evaluation.

2. Experimental

The nickel precursor solution was prepared from nickel acetylacetonate ($\text{Ni}(\text{CH}_3\text{COCHCOCH}_3)_2$, 99.9% purity, Alfa Aesar, Haverhill, MA, USA), which was dispersed in methanol and dissolved in propionic acid to obtain a concentration of 0.6 M. The resulting solution was concentrated by vacuum distillation (at 42 mbar, a bath temperature of 75 °C) to remove excess solvent. Precursor powder was obtained by drying the precursor solution on a hot plate at 80 °C for 15 min. Following this treatment, a green powder was formed, which was subsequently ground to obtain a fine powder suitable for further analysis.

The precursor powder was investigated by thermogravimetric and differential thermal analysis (TG-DTA) in order to evaluate its decomposition behavior. The measurements were carried out in a platinum crucible from room temperature up to 1000 °C, at heating rates of 5, 10 and 15 °C/min, under a static air atmosphere, using a computer-controlled system. Alumina was used as the reference material.

The precursor solution and precursor powder were characterized by means of Fourier-Transform Infrared Spectroscopy (FTIR). FTIR spectra were obtained with a Bruker Tensor 27 FTIR, Bruker Optics GmbH, Ettlingen, Germany) spectrometer in the attenuated total reflection (ATR) mode.

For thin-film preparation, the as-prepared precursor solution was deposited by spin coating onto indium tin oxide (ITO)-coated glass substrates. The films were subsequently thermally treated at 600 °C for holding times of 2, 4, and 6 h under continuous O_2 flow.

The crystalline structures of the films were investigated by X-ray diffraction (XRD) using a Bruker AXS D8 Discover diffractometer. Surface morphology was characterized by atomic force microscopy (AFM; Veeco D3100 (Plainview, NY, USA)), and cross-sectional morphology was examined by scanning electron microscopy (SEM).

The electrochemical redox behavior of a NiO/ITO/glass sample was investigated by cyclic voltammetry (CV) using a three-electrode electrochemical cell. The CV measurements were used to verify reversible $\text{Ni}^{2+}/\text{Ni}^{3+}$ redox activity, while the accompanying color change was assessed qualitatively.

The NiO/ITO/glass system served as the working electrode, while a platinum wire as the counter electrode and an Ag/AgCl electrode as the reference electrode were used as the counter and reference electrodes, respectively. The electrolyte consisted of a 1 M solution of lithium perchlorate (LiClO_4) dissolved in propylene carbonate (PC). The measurements were carried out over a potential window ranging from -0.4 V to $+0.8$ V, at a scan rate of 10 mV/s, and repeated for up to 30 consecutive cycles. All measurements were performed at room temperature under ambient conditions.

3. Results and Discussion

3.1. Physicochemical and Rheological Properties of the Precursor Solution

The rheological properties of the nickel precursor solution were evaluated through contact angle, surface tension, and viscosity measurements (Figure 1). The relatively low contact angle observed on the ITO/glass substrate indicates good wettability (Figure 1a). This behavior favors uniform spreading of the precursor solution and can reduce the formation of pinholes and thickness nonuniformities during film deposition.

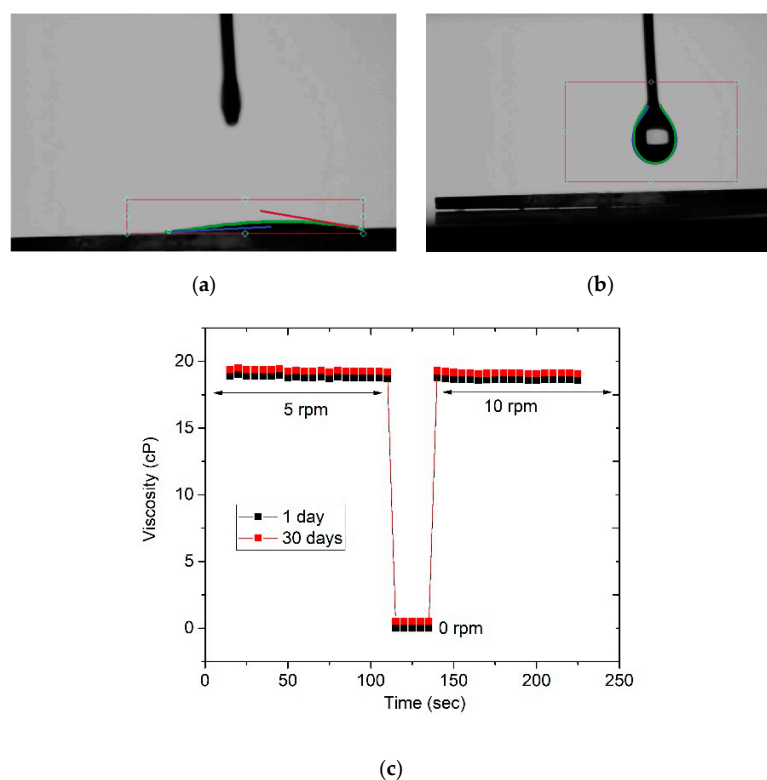


Figure 1. Physicochemical characterization of the nickel precursor solution: (a) contact-angle measurement on the ITO/glass substrate, illustrating the wettability of the precursor solution; (b) pendant-drop measurement used to determine the surface tension; and (c) viscosity as a function of time measured at rotational speeds of 5 and 10 rpm for freshly prepared (1 day, black squares) and aged (30 days, red squares) solutions, demonstrating the temporal stability of the precursor formulation. Surface tension measurements (Figure 1b) indicate a value of approximately 24.9 mN/m, which is considerably lower than that of pure water and consistent with organic solvent systems. The reduced surface tension can be attributed to the presence of methanol and propionic acid, both of which decrease intermolecular cohesion forces. This property improves solution spreading and promotes the formation of continuous, uniform coatings.

The rheological stability of the solution was investigated by viscosity measurements as a function of time (Figure 1c). The results demonstrate that the viscosity remains nearly constant over a period of 30 days, with values of approximately 18–20 cP at rotational speeds of 5 and 10 rpm. This indicates a high degree of temporal stability, with no significant signs of chemical degradation, aggregation, or precipitation occurring in the solution. The slight dependence of viscosity on rotational speed suggests near-Newtonian fluid behavior. The consistency of viscosity over time confirms that the precursor solution maintains its structural integrity and processing characteristics during storage.

3.2. Characterization of Precursor Powder

The thermal behavior of the precursor powder prepared by drying the precursor solution obtained by dissolving nickel acetylacetonate ($\text{Ni}(\text{acac})_2$) in a propionic acid–methanol mixture was investigated by TG-DTA analyses. Similar precursor systems were investigated previously by our group [24], and their thermal decomposition mechanism was discussed in detail. The TG-DTA analysis of the precursor powder was recorded at heating rates of 5, 10, and 15 $^{\circ}\text{C}\cdot\text{min}^{-1}$ (Figure 2a,b). The TG curves show a progressive mass loss occurring in multiple stages up to approximately 500–600 $^{\circ}\text{C}$, followed by a plateau region, indicating the completion of the decomposition process. The total mass loss was approximately 55–60%, which can be attributed to solvent evaporation and the removal of organic components from the propionate-based precursor.

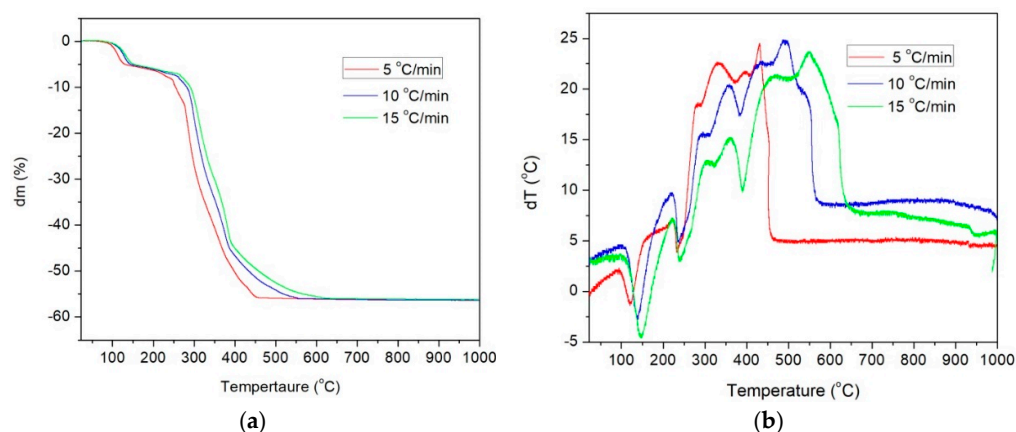


Figure 2. Thermal behavior of the nickel precursor powder recorded at heating rates of 5, 10, and 15 $^{\circ}\text{C}\cdot\text{min}^{-1}$: (a) thermogravimetric curves showing the multistep mass loss associated with solvent removal and decomposition of the organic precursor components; and (b) differential thermal analysis curves showing the corresponding endothermic and exothermic events during precursor conversion.

In the first stage, below ~ 150 $^{\circ}\text{C}$, a small weight loss is observed, corresponding to the evaporation of residual solvent and physically adsorbed water. In the intermediate temperature range (150–350 $^{\circ}\text{C}$), a more pronounced mass loss occurs, associated with melting point of propionate. The DTA curves confirm these transformations, showing several thermal events. Endothermic effects at low temperatures are attributed to solvent evaporation and precursor melting. The major mass loss takes place between 250 and 450 $^{\circ}\text{C}$, where the TG curves exhibit a steep decrease.

This region corresponds to the combustion of the organic fraction and the formation of intermediate species. Above 500 $^{\circ}\text{C}$, the mass remains nearly constant, suggesting the formation of a thermally stable oxide phase, NiO . The strong exothermic peaks observed in the DTA curve in the temperature range of 250–500 $^{\circ}\text{C}$ indicate the decomposition and oxidation of organic species.

An increase in the heating rate leads to a shift in both TG steps and DTA peaks toward higher temperatures, reflecting kinetic limitations in the decomposition process. Despite this shift, the overall decomposition pathway remains unchanged, indicating that the precursor undergoes a similar transformation mechanism regardless of heating rate.

The FTIR spectra of the precursor solution and the corresponding dried precursor powder are presented in Figure 3. The comparison of the two spectra reveals nearly identical vibrational features, indicating that the drying process does not significantly modify the chemical structure of the precursor. The absence of additional absorption bands in the powder spectrum suggests that solvent removal occurs without inducing precursor decomposition or the formation of secondary phases. The characteristic bands observed at approximately 1536 and 1416 cm^{-1} are assigned to the asymmetric and symmetric stretching vibrations of coordinated carboxylate (COO^-) groups. Their presence confirms the coordination of Ni^{2+} ions with propionate ligands, while the separation between the two bands is consistent with a bidentate coordination mode commonly reported for nickel carboxylate complexes.

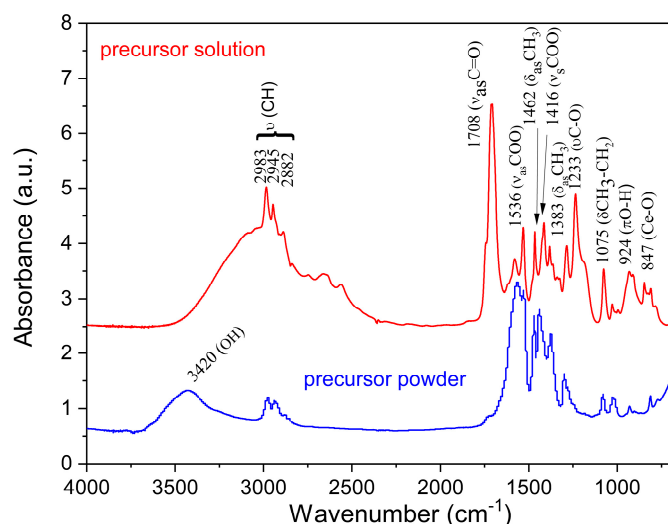


Figure 3. FTIR spectra of the nickel precursor solution and the corresponding dried precursor powder. The bands at approximately 1536 and 1416 cm^{-1} are assigned to the asymmetric and symmetric stretching vibrations of coordinated carboxylate groups, while the bands below 850 cm^{-1} are associated with metal–oxygen vibrations.

Additional bands at approximately 1708, 1462, and 1233 cm^{-1} are attributed to residual propionic acid and correspond to the $\text{C}=\text{O}$ stretching, CH_3 bending, and $\text{C}-\text{O}$ stretching vibrations, respectively. These bands indicate the presence of a small excess of free propionic acid in both the precursor solution and the dried powder. In the low-wavenumber region ($<850 \text{ cm}^{-1}$), weak absorption bands assigned to $\text{Ni}-\text{O}$ vibrations provide further evidence for the formation of metal–oxygen bonds within the precursor structure.

3.3. Characterization of NiO Thin Films

The X-ray diffraction patterns of NiO thin films deposited on ITO/glass substrates and thermally treated at 600 $^{\circ}\text{C}$ for different holding times (2, 4, and 6 h) are presented in Figure 4. The diffraction peaks observed at approximately $2\theta \approx 37^{\circ}$, 43° , and 63° can be indexed to the (111), (200), and (220) crystallographic planes of cubic NiO (JCPDS 4-0835), confirming the formation of the polycrystalline NiO phase. No secondary phases or intermediate compounds were detected, indicating the complete decomposition of the precursor and the successful formation of single-phase NiO. In addition to the NiO reflections, the peaks marked with asterisk correspond to the underlying ITO/glass substrate.

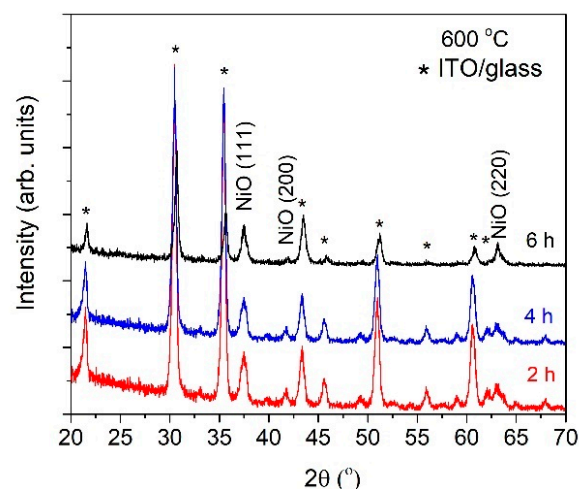


Figure 4. X-ray diffraction patterns of NiO thin films deposited on ITO-coated glass and thermally treated at 600 °C for holding times of 2, 4, and 6 h. The reflections indexed as NiO(111), NiO(200), and NiO(220) confirm the formation of polycrystalline cubic NiO, while the peaks marked with an asterisk originate from the ITO/glass substrate. Quantitative analysis of the NiO(111) reflection indicated crystallite sizes of 12.4, 13.2, and 13.9 nm for holding times of 2, 4, and 6 h, respectively.

To quantitatively assess the influence of holding time on crystallite size, the average crystallite size was calculated from the NiO(111) reflection using the Scherrer equation, $D = K\lambda/(\beta \cos \theta)$, where $K = 0.9$, $\lambda = 1.5406 \text{ \AA}$ (Cu $K\alpha$), and β is the full width at half maximum (FWHM) obtained by Gaussian peak fitting after linear background subtraction. The calculated crystallite sizes were 12.4 nm, 13.2 nm, and 13.9 nm for the films treated for 2, 4, and 6 h, respectively.

Contrary to a purely qualitative inspection of peak broadening, this quantitative analysis reveals a progressive increase in crystallite size with increasing holding time, accompanied by a corresponding narrowing of the NiO(111) reflection (FWHM decreasing from 0.68° at 2 h to 0.61° at 6 h). This trend suggests that prolonged thermal treatment promotes grain growth and coarsening of the NiO crystallites, rather than a reduction in crystallite size or an increase in structural disorder. Overall, the XRD results demonstrate that the thermal treatment at 600 °C is sufficient to obtain phase-pure NiO thin films, with holding time acting as an effective parameter for tuning crystallite size rather than compromising film crystallinity.

The morphology of the films was characterized using atomic force microscopy (Figure 5). The investigated films exhibit a uniform and homogeneous surface morphology, without visible defects such as cracks, pinholes, or large agglomerations, indicating the good quality of the deposited layers. The surface is composed of fine and uniformly distributed grains, suggesting the formation of nanostructured NiO films. A comparison between the samples shows only minor changes in surface topography with increasing annealing time. The film treated for 2 h and 4 h exhibit a continuous, smooth and compact morphology. The 6 h sample shows a slight increase in surface irregularity.

Thus, the obtained films are uniform, with small crystallite sizes, and display low root-mean-square (RMS) roughness values of 2.5, 2.5, and 2.7 nm, corresponding to NiO films subjected to holding times of 2, 4, and 6 h, respectively.

Cross-sectional SEM imaging (Figure 6) was used to determine film thickness. The NiO film treated for 6 h exhibits a thickness of approximately 320 nm, revealing a dense, columnar microstructure with fine surface texture, consistent with the low RMS roughness values measured by AFM. This thickness is comparable to values reported for solution-processed electrochromic NiO thin films [11,13,21].

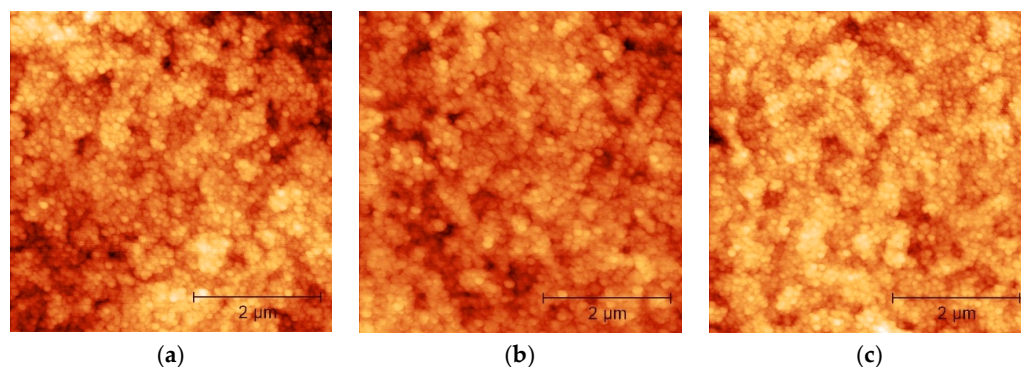


Figure 5. AFM surface-topography images of NiO thin films thermally treated at 600 °C for holding times of (a) 2 h, (b) 4 h, and (c) 6 h. All films exhibit continuous and homogeneous surfaces composed of fine nanoscale features. The corresponding RMS roughness values were 2.5, 2.5, and 2.7 nm for the 2, 4, and 6 h samples, respectively.

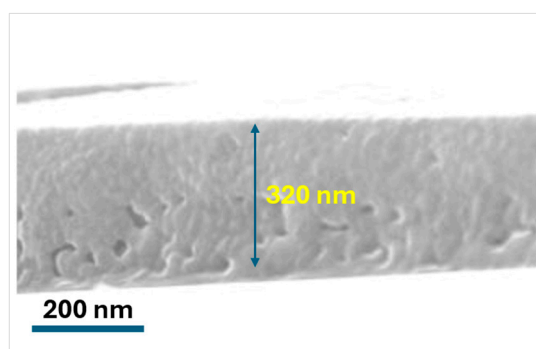


Figure 6. Cross-sectional SEM image of the NiO thin film thermally treated at 600 °C for 6 h. The film exhibits a thickness of approximately 320 nm and a dense, columnar microstructure. The marked vertical dimension indicates the measured film thickness, while the scale bar corresponds to 200 nm.

3.4. Electrochemical Tests

The electrochemical redox behavior of the NiO/ITO/glass sample heat treated at 600 °C, for 6 h was investigated by cyclic voltammetry (CV), as illustrated in Figure 7. The measurements were performed in a three-electrode electrochemical cell (Figure 7c), using the NiO/ITO/glass system as the working electrode, within a potential window ranging from −0.4 V to +0.8 V, at a scan rate of 10 mV/s. Voltammograms were recorded for the 1st, 20th, and 30th cycles and compared against the background current of the bare ITO/glass substrate.

As shown in Figure 7a, all voltammograms display a single dominant redox couple, consistent with the reversible $\text{Ni}^{2+}/\text{Ni}^{3+}$ transition. In the first cycle, the anodic oxidation peak appears at approximately +0.28 V, while the cathodic reduction peak is located near 0.0 V, with relatively modest current densities. Upon cycling, both the anodic and cathodic peak currents increase substantially—from cycle 1 to cycles 20 and 30—while the peak positions shift slightly outward, resulting in a progressive increase in the peak-to-peak separation (ΔE). This behavior is characteristic of an activation process, in which repeated electrochemical cycling gradually improves ion insertion/extraction kinetics within the NiO matrix, likely through the progressive development of a more accessible $\text{Ni}(\text{OH})_2/\text{NiOOH}$ interfacial layer. Within the 30-cycle window investigated here, the NiO/ITO/glass system exhibits a clear activation behavior, characterized by a progressive increase in peak current and charge density from cycle 1 to cycle 30. This is consistent with the initial activation stage typically reported for NiO-based electrochromic films prior to the onset of steady-state cycling and eventual degradation at extended cycle numbers.

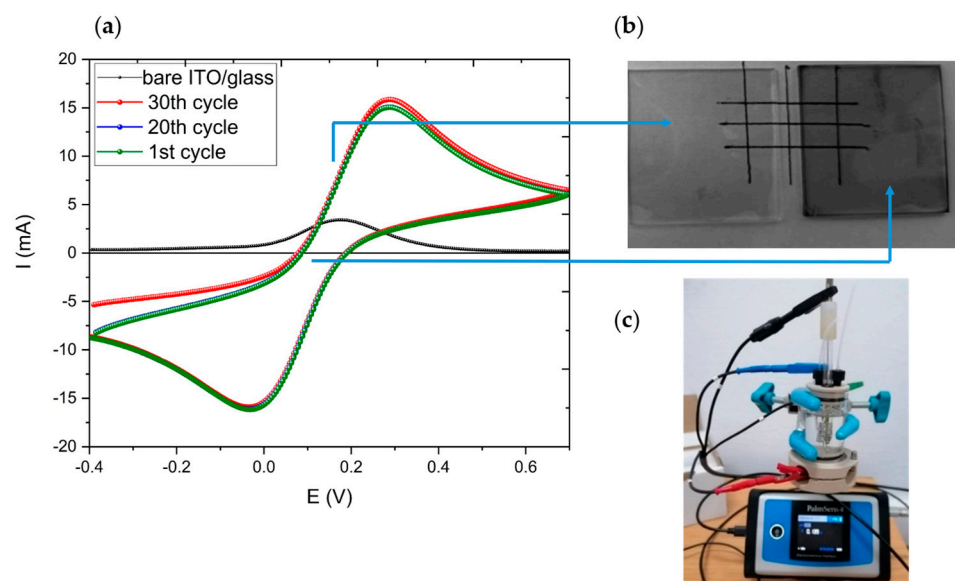
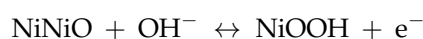


Figure 7. Electrochemical characterization of the NiO/ITO/glass sample heat treated at 600 °C, for 6 h: (a) cyclic voltammograms recorded for the 1st, 20th, and 30th cycles in 1 M LiClO₄ dissolved in propylene carbonate, within a potential range of −0.4 to +0.8 V at a scan rate of 10 mV s^{−1}, together with the response of the bare ITO/glass substrate; (b) photographs of the NiO film in the bleached and colored states, showing the qualitative visible color change associated with the Ni²⁺/Ni³⁺ redox process; and (c) three-electrode electrochemical measurement setup used for cyclic-voltammetry testing.

The electrochromic nature of the NiO films is directly evidenced in Figure 7b, which shows photographs of the same film in its two distinct optical states: the bleached, transparent state and the colored, brown state. During electrochemical cycling, the film changes to the brown state during anodic oxidation (Ni²⁺ → Ni³⁺) and returns to the transparent state during cathodic reduction (Ni³⁺ → Ni²⁺). This visible optical contrast confirms the functional electrochromic response of the deposited NiO films.

According to literature, the dominant redox processes underlying this electrochromic behavior may be attributed to the following electrochemical reactions [18,19,25–27]:



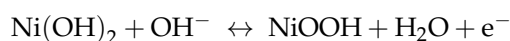
or



and



or



The evolution of the voltammograms over multiple cycles indicates that the overall nature and morphology of the films undergo only minor structural changes during cycling, as evidenced by the well-preserved peak shape and the absence of new electrochemical features. Nevertheless, the progressive increase in both anodic and cathodic currents between cycle 1 and cycles 20–30 confirms a continuous enhancement of the electrochemical activity, suggesting that the number of electrochemically active sites and consequently the number of protons and electrons incorporated into the film increases with cycling. The lifetime behavior of the NiO/ITO/glass system in the electrolyte can thus be described by

three sequential stages: an alka activation period, a steady-state regime, and an eventual degradation stage at extended cycling.

The electrochemical parameters obtained in the present study are in good agreement with those reported in the literature for NiO-based electrochromic thin films (Table 2).

Table 2. Comparison of preparation methods and electrochromic characteristics of NiO-based thin films.

Material	Deposition Method	Substrate	Electrolyte	Potential Window (V)	Scan Rate (mV/s)	Anodic Peak (V)	Color Change	Ref.
NiO	CSD	ITO/glass	1 M LiClO ₄ /PC	−0.4 to +0.8	10	~+0.28	Transparent ↔ Brown	This work
NiO	Sol–gel dip coating	ITO/glass	1 M KOH	—	—	—	Transparent ↔ Brown	[11]
NiO (porous)	Chemical bath deposition	ITO/glass	1 M KOH	−0.1 to +0.7	50	—	Transparent ↔ Brown	[16]
NiO	RF magnetron sputtering	ITO/glass	1 M LiClO ₄ /PC	—	—	—	Transparent ↔ Brown	[28]
NiO	DC reactive magnetron sputtering	ITO/glass	1 M KOH	—	—	—	Transparent ↔ Brown	[29]
Li-doped NiO	Hydrothermal	ITO/glass	1 M LiOH	−0.5 to +1.0	50	~+0.7	Transparent ↔ Dark brown	[12]
NiO	Electrodeposition + thermal oxidation	FTO/glass	1 M LiClO ₄ /PC	—	30	—	Transparent ↔ Brown	[30]
Co-doped NiO	Sol–gel spin coating	ITO/glass	1 M KOH	—	—	—	Transparent ↔ Brown	[31]

The anodic oxidation peak at approximately +0.28 V and the cathodic reduction peak near 0.0 V, recorded in 1 M LiClO₄/propylene carbonate (PC) at 10 mV/s, are consistent with values reported for NiO films cycled in non-aqueous LiClO₄/PC electrolytes, where the oxidation peak is typically centered around +0.3 V. In contrast, NiO films investigated in aqueous alkaline electrolytes such as KOH or LiOH exhibit anodic peaks at significantly higher potentials (+0.5 V to +0.7 V), reflecting the dominance of OH[−] intercalation in aqueous media compared to the Li⁺ insertion mechanism characteristic of organic electrolytes. From a methodological perspective, the chemical solution deposition route via spin coating employed in this work represents a cost-effective and scalable alternative to physical vapor deposition techniques such as RF or DC magnetron sputtering, while offering comparable electrochemical performance and uniform film formation, as confirmed by the low RMS roughness values obtained by AFM. The reversible brown-to-transparent color switching confirmed in this work is characteristic of anodic NiO electrochromism and consistent with all comparable systems reported in the literature, regardless of deposition method or electrolyte composition.

4. Conclusions

NiO thin films were successfully prepared on ITO/glass substrates by chemical solution deposition using spin coating from a nickel acetylacetonate-based precursor, followed by thermal treatment at 600 °C under an oxygen atmosphere.

TG-DTA and FTIR analyses characterized the precursor decomposition and confirmed the formation of nickel–oxygen bonding through propionate coordination, with no significant chemical changes occurring during drying. X-ray diffraction demonstrated the formation of phase-pure, polycrystalline cubic NiO without detectable secondary phases.

AFM investigations revealed homogeneous, crack-free surfaces with low roughness values, indicating good film continuity and uniformity. Quantitative analysis of the NiO(111) reflection showed a modest increase in crystallite size from 12.4 to 13.9 nm as the holding time increased from 2 to 6 h, while AFM indicated only minor changes in surface roughness and morphology. Cross-sectional SEM showed a film thickness of approximately 320 nm for the sample annealed for 6 h. Overall, prolonged annealing promoted limited crystallite growth but did not produce substantial changes in surface morphology.

Cyclic voltammetry confirmed reversible $\text{Ni}^{2+}/\text{Ni}^{3+}$ redox activity in the investigated NiO/ITO/glass sample, accompanied by qualitative switching between bleached and colored states. Because comparative electrochemical measurements were not obtained for all holding times, no direct conclusion can be drawn regarding the effect of annealing duration on electrochemical performance.

The electrical integrity of the ITO substrate after thermal treatment at 600 °C was not directly quantified via sheet resistance measurements; however, the reproducible electrochemical response observed across repeated CV cycles indicates that the substrate retained sufficient conductivity for electrochemical testing.

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Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author. The data are not publicly available due to ongoing research and future publications based on the same dataset.

Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

The following abbreviations are used in this manuscript:

AFM	Atomic Force Microscopy
ATR	Attenuated Total Reflection
CV	Cyclic Voltammetry
DTA	Differential Thermal Analysis
FTIR	Transform Infrared Spectroscopy
ITO	indium-doped tin oxide
RMS	Root Mean Square
TG	Thermogravimetric
XRD	X-ray Diffraction

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