

Article

Unveiling Nanogranular Advancements in Nickel-Doped Tungsten Oxide for Superior Electrochromic Performance

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Abstract: Electrochromic materials allow for precise control of their optical properties by applying an electric field, which has led to recent developments in energy-saving and indoor temperature control systems like smart windows. The selective incorporation of metal dopants is an effective technique for generating highly advanced semiconducting metal oxides with precisely customized physicochemical characteristics. In this report, we employed a one-step electrodeposition process to fabricate nickel-doped tungsten oxide (W–Ni) thin films, systematically probing the impact of nickel (Ni) doping on the collective material characteristics. Comprehensive X-ray diffraction research revealed significant changes in diffraction patterns, suggesting slight modifications in the structure caused by Ni doping. The scanning electron microscopy showed complex differences in the microstructure of the film, such as a dense surface, porosity, and clustering of nanogranules. The WNi-3% thin film doped at 3 wt. % exhibited excellent electrochromic performance by efficiently handling lithium ions and displaying favorable electrochromic properties. The improved electrode, WNi-3%, showed a maximum optical modulation of 81.90%, exceptional reversibility of 99.4%, and a high coloration efficiency of 75.12 cm²/C. These findings underscore the efficacy of Ni-doping in tailoring the electrochromic properties of nickel-doped tungsten oxide thin films, thereby advancing the frontiers of high-performance electrochromic materials for energy-efficient applications.

Keywords: thin film; tungsten oxide; electrodeposition; doping; nanogranules; electrochromism



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1. Introduction

Population growth and economic development over the last several decades have led to a steady increase in the demand for energy worldwide. The sustainable progress of human civilization is threatened by the depletion of fossil fuels such as coal, crude oil, and natural gas [1–4]. In order to address the present resource crises and environmental issues that contemporary civilization is facing, it is essential to focus on finding clean energy sources that are safe, inexpensive, and ecologically benign [4–8].

The electrochromic (EC) effect is a phenomenon in which the optical properties of EC materials undergo a transition when subjected to an applied electric field force, which was initially reported by Deb et al. in 1969 [9]. When exposed to external electric field forces, microscopic examination includes the reversible process of extracting or injecting ions and electrons into these materials [10–14]. Consequently, EC materials have received significant attention and research, leading to the invention of electrochromic devices (ECDs). Numerous research studies have shown that ECDs are being intensively investigated for prospective applications in a variety of fields, including smart windows, automated anti-glare rearview mirrors, spaceship thermal management, and sensors [8].

EC materials are categorized into three main groups: metal oxides, conductive polymers, and inorganic non-oxides. Metal oxides including WO₃, NiO, Nb₂O₅, TiO₂, MnO₂, and V₂O₅

are widely used and promising options [10,12]. Extensive research has been dedicated to tungsten oxide (WO_3) for its recognized ability to function as a material with outstanding EC properties. However, typical WO_3 materials have limited practical applications due to insufficient EC performance including limited optical contrast and restricted diffusion of ions [8,15,16]. Thus, in recent years, researchers have been focused on enhancing the EC properties of WO_3 . The effective integration of doped metal atoms into active materials increases electrical conductivity and forms charge barriers within their crystal structures. Improved EC performance resulting from structural changes to materials is largely attributable to this intentional introduction [17]. As a result, this change improves conductivity and creates barriers that boost several processes involving charges. Experiments have been conducted to improve the EC performance of WO_3 by adding a variety of metal atoms, including Ti, Zn, Mo, Eu, Fe, and Ni [18]. As an example, Meng et al. discovered that the state density of monoclinic WO_3 is improved by the addition of Ni doping, which ultimately leads to an enhancement in the crystal structure's ability to transmit electrical current [19]. Using the DC co-sputtering process, Green et al. developed Ni- WO_3 films and discovered that in order to improve the optical modulation of WO_3 films, a low concentration of Ni doping was necessary [20,21]. O-Rueda de Leon et al. employed spray pyrolysis to create Mo-doped WO_3 layers on fluorine-doped tin oxide (FTO) glass. The best electrochromic reaction was seen in WO_3 films that had 6.0 wt. % Mo doping. Alternatively, it was found that about 2.0 wt. % Mo was the best amount of doping to achieve the highest level of electrical stability [22]. Recently, Cai et al. added Ti doping to the WO_3 nanostructure and used chemical processes to make a film with star-shaped Ti doping in the WO_3 nanostructure. The positive traits of these films included low charge transfer resistance, high color efficiency, and fast change speed. Even so, the optical modulation that was achieved (49.1% at 750 nm) was not as good as what is usually seen in amorphous films (67.6% at 632 nm). Numerous studies have concentrated on nickel (Ni) as it is considered an excellent dopant for WO_3 . This is attributed to the similarity in atomic radii (0.060 nm for Ni and 0.062 nm for W) and favorable oxidation states (Ni^{2+} and Ni^{4+}), making it beneficial for enhancing the electrochromic activity of WO_3 -based nanomaterials [23].

The objective of this work was to streamline the fabrication procedure of nickel-doped tungsten oxide (Ni-doped WO_3) thin films on FTO glass substrates by using an electrodeposition technique. A thorough analysis was performed on WO_3 thin films with different degrees of Ni doping in order to specify the most optimized Ni dopant concentration and gain a deeper understanding of its influence on the structural, morphological, and electrochromic (EC) characteristics of WO_3 thin films. The incorporation of Ni by doping causes changes in the electrical band alignment of the material, resulting in a displacement of the electron energy levels inside the bandgap of WO_3 . This has a direct impact on the electrical conductivity, optical properties, and the material's capacity to control the passage of light. In addition, the inclusion of Ni dopant may affect the speed and effectiveness of the ion intercalation and deintercalation processes, therefore improving the color contrast characteristics of the material. Moreover, the route of doping may enhance the rate at which ions diffuse, thus improving the whole EC performance of the material. In a similar way, doping enhances the material's characteristics by introducing more redox reaction sites.

2. Experimental

2.1. Chemicals

No further processing was necessary for any of the chemicals and solvents as they were all of analytical grade (AR). We sourced the FTO-containing glass from MTI Co., Ltd. in South Korea. After pre-cleaning the conducting FTO glass using ethanol, acetone, and distilled water for 15 min each, the substrate was used for the further deposition process. The sodium tungstate dihydrate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$), 30% H_2O_2 , nitric acid (HNO_3), nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), lithium perchlorate (LiClO_4), and propylene carbonate (PC) were all provided by Sigma-Aldrich U.S.

2.2. Fabrication of Ni-Doped WO₃ Thin Films

Ni-doped WO₃ (W-Ni) thin films were synthesized utilizing a simple electrodeposition method. A 15 mM solution of Na₂WO₄·2H₂O was synthesized in 100 mL of deionized (DI) water. Afterward, the addition of 0.5 mL of 30% H₂O₂ took place to produce a bright, yellow-colored solution. Then, HNO₃ was added while the mixture was heated to 45 °C. A further step involved bringing the resulting peroxy-tungstic acid (PTA) solution to room temperature [9]. Pre-cleaned FTO substrates were subjected to electrochemical deposition, and varied concentrations of Ni doping (1, 3, 5 wt. %; designated as WNi-1%, WNi-3%, and WNi-5%, respectively) were added to produce distinct compositions. This work examined the effects of different Ni doping levels on the structure, composition, and EC characteristics of the material. Figure 1 displays a detailed schematic depiction of the W-Ni synthesis process.

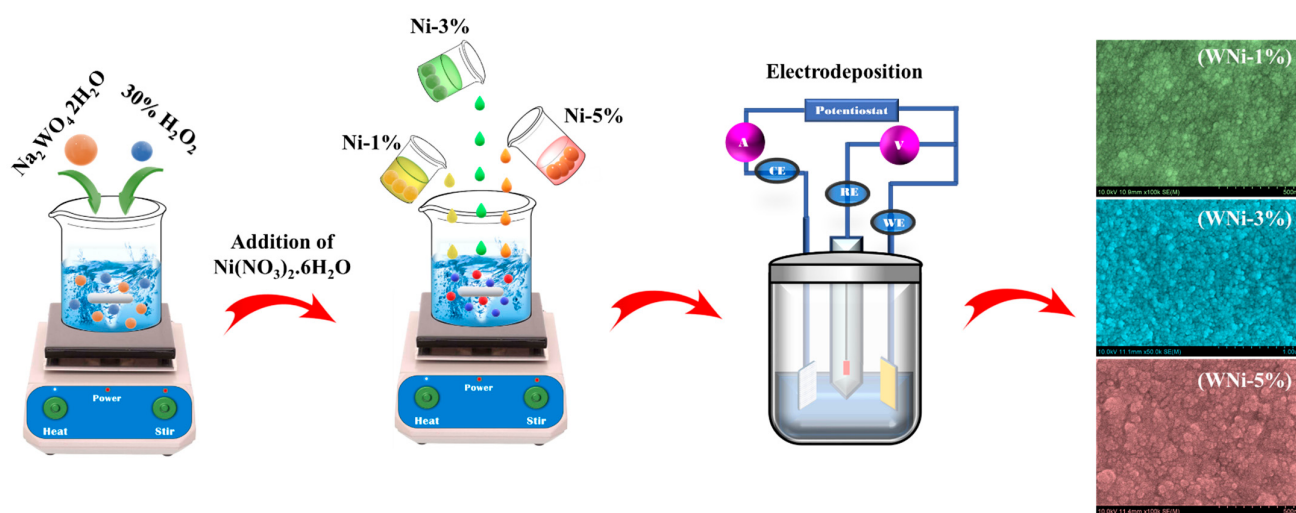


Figure 1. Detailed schematic depiction of the W-Ni synthesis process.

2.3. Electrochromic Device Fabrication

A simple electrodeposited W-Ni thin film was then used to demonstrate EC practical application. In this investigation, glass/FTO/WNi-3%/LiClO₄ + PC/FTO/glass with dimensions of 4 × 3 cm² was utilized to construct the device. The FTO glass substrate acted as a conducting electrode; the WNi-3% thin film deposited on FTO glass was used as the EC active layer; and 1 M LiClO₄ + PC was used as an electrolyte to sandwich the active layer of deposited FTO and bare FTO/glass substrate. The sandwich-style EC assembly was completely sealed using transparent double-sided adhesive tape (Scotch Brand Tape, 3 M).

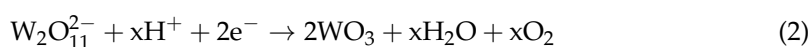
3. Sample Characterization and Electrochromic Measurements

X-ray diffraction (XRD; PAN analytical) was employed using Cu-Kα radiation to evaluate the structural properties and phase integrity of the W-Ni thin films. Field-emission scanning electron microscopy (FE-SEM, S-4800 HITACHI, Ltd., Tokyo, Japan) with an energy-dispersive spectroscopy (EDS) was used to analyze the morphology and chemical composition of the thin films. Raman spectroscopy was performed using an Xplora (Horiba) micro-Raman spectrophotometer with a changed-couple device detector and a 532 nm (2.33 eV) excitation source. The exact elemental composition and oxidation state of the elements were studied using X-ray photoelectron spectroscopy (XPS; K-Alpha, Thermo Scientific, Swindon, UK). All of the EC measurements were conducted using a battery cycler (Biologic Instrument-WBCS3000) in a three-electrode configuration with W-Ni thin film, platinum, and Ag/AgCl as the working, counter, and reference electrodes, respectively. The electrolyte employed for the Li⁺ ion source was 1 M LiClO₄ + PC. The analysis of the in situ optical transmittance in the colored and bleached state was taken using a UV-Vis spectrophotometer (Model: S-3100, SCINCO) linked to an electrochemical workstation (IVIUM Technologies, COMPACTSTAT).

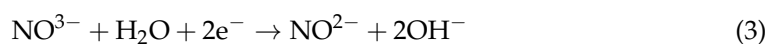
4. Results and Discussion

4.1. Mechanism of Electrodeposition

The synthesis mechanism of electrodeposited Ni-doped WO₃ involves several steps, including the preparation of the electrolyte solution, electrodeposition process, and deposition parameters. During electrodeposition, tungsten and nickel ions from the electrolyte solution were reduced at the surface of the working electrode (FTO substrate), leading to the formation of Ni-doped WO₃ nanograins. Throughout electrodeposition, the cathodic (negative) current is acquired as a function of time, giving insights into the kinetics of the process. The electrodeposition mechanism for WO₃ can be explained as follows: firstly, W₂O₁₁^{2−} ions were generated by dissolving aqueous H₂O₂ in sodium tungstate solution. Then, W₂O₁₁^{2−} ions were reduced to HxWO₃ under acidic conditions. Lastly, the HxWO₃ was oxidized to transparent WO₃ in the electrolyte solution with open-circuit potential [11,16].



For the doping of nickel, the electrochemical reduction of Ni(NO₃)₂·6H₂O occurred. The reduction resulted in the generation of excess hydroxyl ions, followed by the formation of Ni-doped WO₃ [24].



4.2. X-ray Diffraction (XRD) Elucidation

X-ray diffraction (XRD) was employed to scrutinize the structural attributes of W-Ni thin films. All of the W-Ni thin films showed an amorphous structure, as illustrated in Figure 2, where discernible peaks representative of the FTO substrate were evident across all samples. Within the lower 2θ range, approximately at 26° 2θ, a broad hump was identified, signifying the amorphous nature of WO₃. The non-appearance of supplementary diffraction peaks attributed to WO₃ implied the presence of an amorphous nature within the films [9,24]. Despite a uniform XRD pattern orientation observed in all samples, a subtle discrepancy in the intensity of the noted hump was observed. This consistency in XRD pattern orientation suggested homogeneity in the structural attributes among the W-Ni thin films. No peaks corresponding to Ni were detected for any W-Ni thin film [25,26]. Amorphous WO₃ thin films are commonly favored for electrochromic applications. Their suitability arises from their tightly packed and highly crystalline structure, which hinders ion diffusion, thereby leading to a slower response time. In contrast, the amorphous WO₃ coating exhibits rapid switching kinetics and substantial optical modulation due to its loosely packed crystal structure and ample specific surface area [27,28].

4.3. Raman Spectroscopy Analysis

W-Ni thin films present a compelling avenue for electrochromic applications, and the investigation of their bleached and colored states through Raman spectroscopy yields valuable insights into their structural transformations. Figure 3a illustrates the Raman spectra acquired in the bleached state across different concentrations of Ni dopants (WNi-1%, WNi-3%, and WNi-5%). Within the spectral range, two distinct peaks at 241 cm^{−1} and 305 cm^{−1} are traced, corresponding to the angular vibration modes of O-W-O interactions [29,30]. The characteristic attribute of amorphous WO₃ is shown through broadened peaks centered at 633–680 cm^{−1} and 955 cm^{−1}, originating from the stretching vibrations associated with W=O and W-O modes, respectively [31]. The supplementary band identified within the 1094 cm^{−1} range is attributed to the FTO substrates [32]. Figure 3a reveals an absence of Raman bands associated with impurities. A subtle shift in peak position, coupled with a decrease in peak intensity, was observed in correlation with the increase

in the Ni dopant concentration. This phenomenon may be explained by the probable creation of structural surface imperfections caused by the introduction of the foreign element (Ni) [30,32]. These observations contribute to an understanding of the structural dynamics and interaction modes present in W-Ni thin films during their bleached state, paving the way for comprehensive electrochromic assessments.

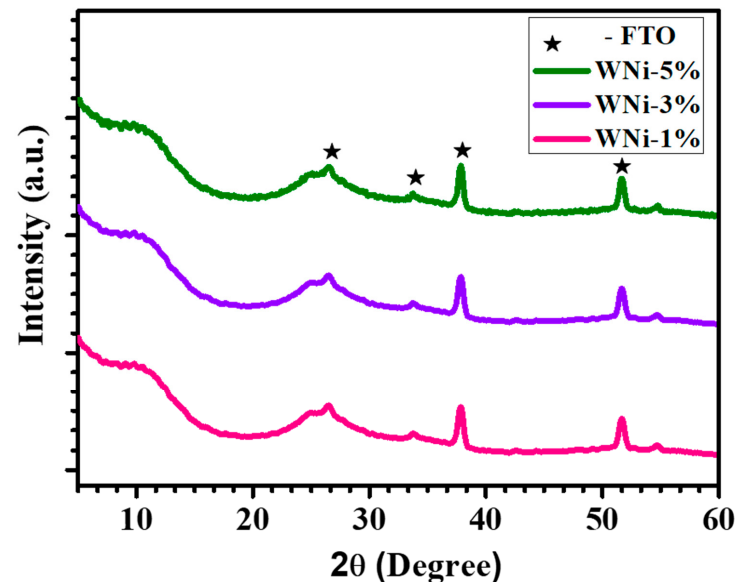


Figure 2. XRD pattern of WNi-1%, WNi-3%, and WNi-5% samples prepared by electrodeposition technique.

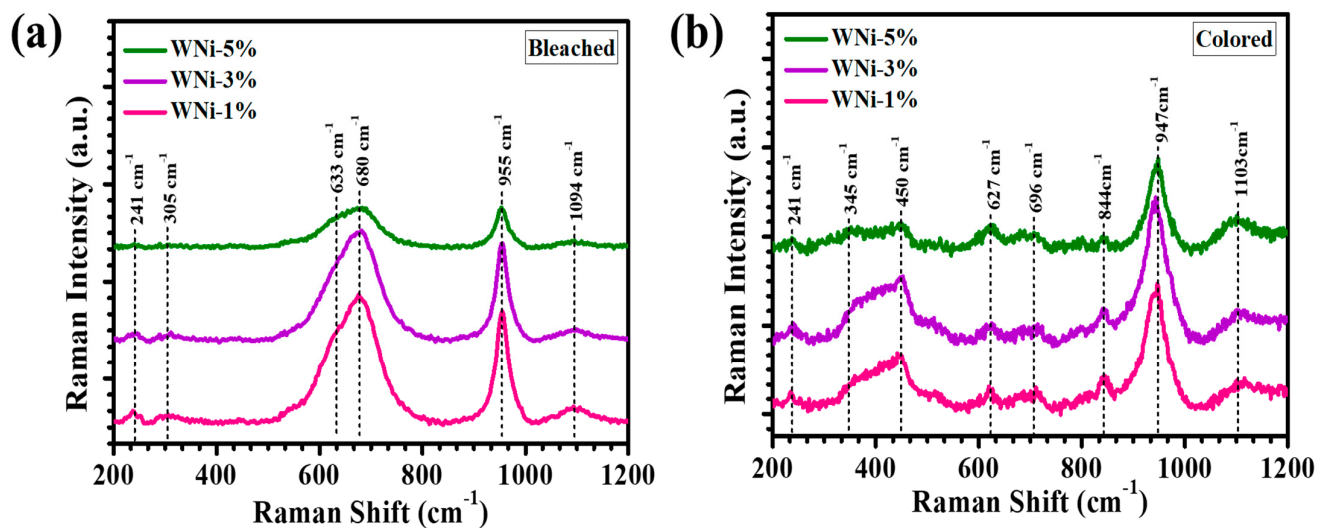


Figure 3. Combined Raman spectra of bleached and colored state WNi-1%, WNi-3%, and WNi-5% thin films.

Figure 3b shows the Raman spectra obtained in the colored state, which clearly display identifiable vibrational modes related to the introduction of Li^+ ions into W-Ni thin films. The coloration process induces a phase transition in the material, leading to the formation of the $\text{Li}_y(\text{W}_{1-x}\text{Ni}_x)\text{O}_3$ phase [9,33]. Consequently, pronounced shifts in spectral bands relative to the bleached state Raman spectra are observed, accompanied by the emergence of an additional number of Raman peaks. The observed peak shifts are attributed to lattice distortions arising from lithium intercalation [34]. Moreover, new peaks at 345 cm^{-1} , 450 cm^{-1} , and 844 cm^{-1} are identified, corresponding to the $\text{Li}_y(\text{W}_{1-x}\text{Ni}_x)\text{O}_3$ phase [35].

Realizing the structural modifications in electrodes during the colored state elucidates the complete phase transition of the material, underlying the electrochromic behavior exhibited by W-Ni thin films.

4.4. X-ray Photoelectron Spectroscopy (XPS) Elucidation

X-ray photoelectron spectroscopy (XPS) was applied to ascertain the presence of the targeted elements and elucidate their specific valence states within the synthesized material. As depicted in Figure 4a, the survey spectrum of the WNi-3% sample clearly confirms the existence of W, Ni, and O elements, along with discernible peak attributed to residual carbon originating from environmental sources. The distinctive peaks corresponding to W, Ni, and O in the survey spectrum serve as elemental indicators, supporting the successful electrodeposition of the W-Ni thin film. A more detailed examination of the core-level XPS spectra for W4f, presented in Figure 4b, unveils two prominent peaks positioned at 35.44 eV and 37.54 eV, corresponding to the W4f_{7/2} and W4f_{5/2} orbitals, respectively. The identification of these peaks at their respective energy levels conclusively establishes the predominant valence state of W as W⁶⁺, affirming the tungsten's state in WO₃ [36]. The Ni2p XPS spectra for WNi-3% are illustrated in Figure 4c, revealing a spectrum characterized by irregular noise peaks, in which broad main and satellite peaks were detected. The primary peak at a binding energy of 856.1 eV corresponds to Ni2p_{3/2}, while the peak at 864 eV is associated with its satellite peak. Another significant peak at 874.2 eV represents Ni2p_{1/2}, with its corresponding satellite peak situated at 880 eV [37]. The difference in binding energy between the principal peaks of Ni2p_{3/2} and Ni2p_{1/2}, approximately 18.1 eV, precisely aligns with the reported data for Ni, providing compelling evidence for the successful integration of Ni ions into the host matrix of WO₃ nanogranules in the form of Ni²⁺ [36]. Additionally, the O1s spectra depicted in Figure 4d exhibit a prominent peak centered at 530.2 eV, attributed to metal–oxygen bonds in the oxidation state of O²⁺. A supplementary shoulder peak at 531.9 eV indicates the presence of hydroxyl groups (OH[−]) [38].

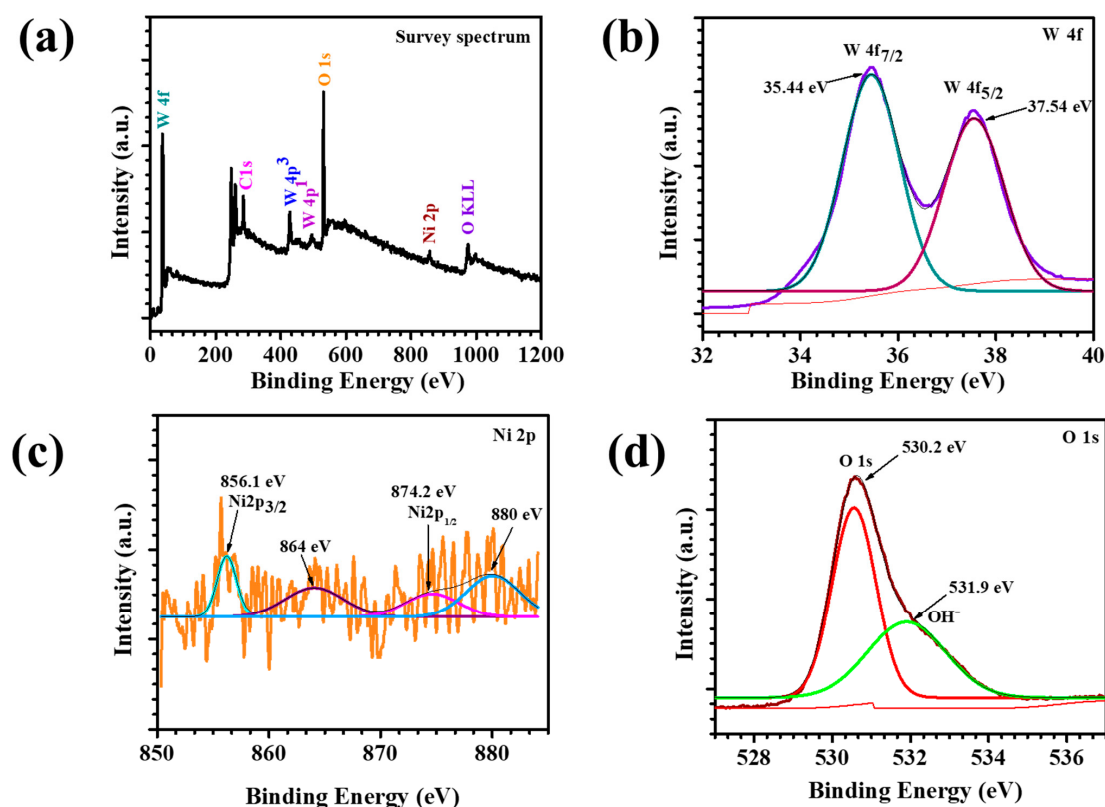


Figure 4. (a) High-resolution XPS survey spectra (b) W 4f spectra (c) Ni 2p spectra and (d) O 1s XPS core level of WNi-3% thin film.

4.5. Morphological and Elemental Compositional Characteristics

Surface morphology plays a crucial role in dictating electrochemical performance, offering valuable insights into the electrode–electrolyte interaction in electrochemical measurements. In this study, we examined how various Ni doping concentrations influence the controlled growth of distinct morphologies. The surface morphology of WNi-1%, WNi-3%, and WNi-5% thin films are shown in Figure 5a–c at two distinct magnifications of 50 kX and 100 kX. The structure and morphology of these materials are influenced by factors such as dopant type, amount, and fabrication method. Consequently, the surface morphologies of the WO₃ films exhibit variation with increasing Ni content. The films exhibit uniform adherence to the FTO substrate, forming nanoparticles.

At a minimal 1% Ni doping Figure 5a,a1, nanogranules are small and tightly clustered, forming a dense network covering the WNi-1% substrate. Conversely, the surface structure underwent considerable alteration with a rise in doping concentration from 3 and 5%. Figure 5b,b1 shows an interconnected nanogranule that led to the formation of a porous structure for the WNi-3% sample. The interconnected porous structure significantly enhances the kinetics of ions and electrons transport by providing conductive and smooth pathways. In Figure 5c,c1, the WNi-5% thin film exhibited compact spherical bunches due to the agglomeration of nanogranules. This agglomeration restricts the electrode–electrolyte interaction due to the granules' complete aggregation and low porosity [9].

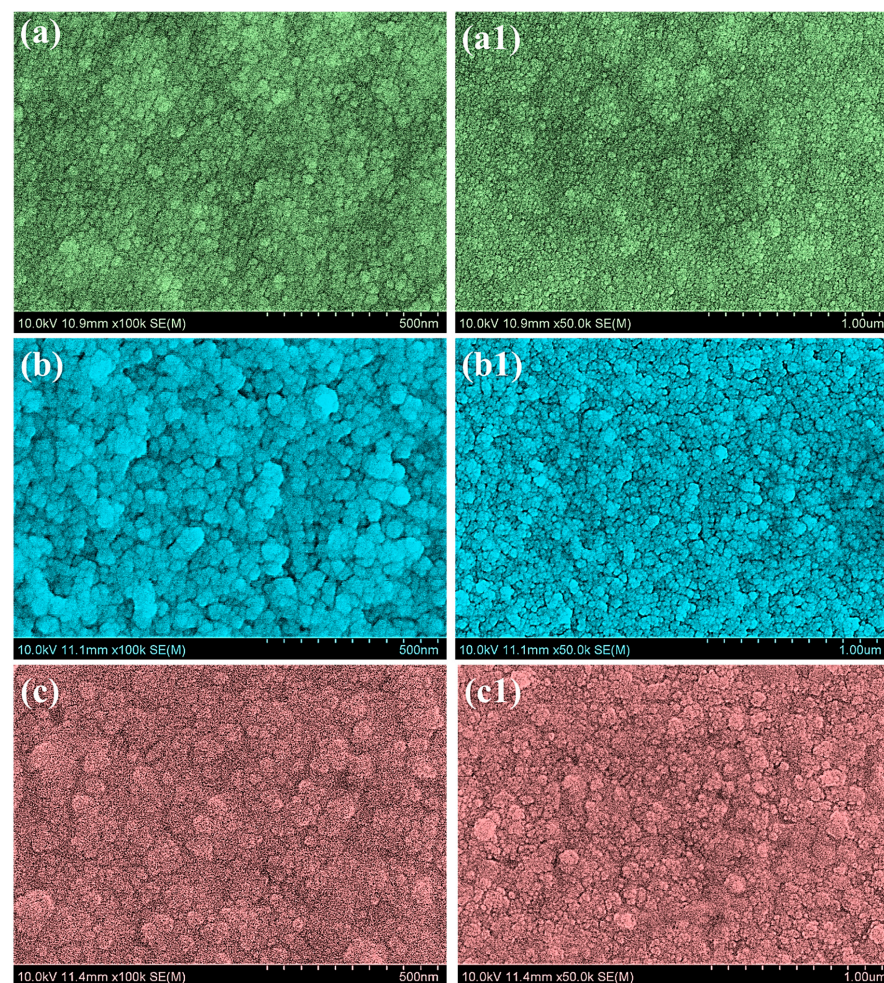


Figure 5. FE-SEM images of (a,a1) WNi-1%, (b,b1) WNi-3%, and (c,c1) WNi-5%, thin films.

The observed morphological variation in the thin films was influenced by varying Ni content. At 1% Ni doping, the clustered morphology likely arises from the initial stage of Ni incorporation. With a low concentration, individual Ni atoms may nucleate pref-

entially on the surface, leading to the formation of small clusters. These clusters may aggregate due to surface diffusion and coalescence processes, resulting in the observed dense cluster morphology. On increasing the Ni content to 3%, an interconnected and consistent nanogranule arrangement was observed. The increased Ni content promotes the increased surface diffusion of Ni atoms across the film surface; as a result, the material can efficiently migrate and unite into nanogranules. Additionally, this optimum Ni concentration is sufficient to facilitate the nucleation and growth of nanogranules without inducing excessive aggregation. While at 5% doping, the compact spherical bunches formed suggest a saturation point at which further Ni incorporation leads to densification of the WO_3 film. The higher Ni concentration may inhibit the growth of large nanogranules, promoting compaction of the film structure [30,39,40]. Overall, the morphological investigations reveal that the WNi-3% sample has an interconnected nanogranular arrangement with a porous structure. The porous structure of this material increases the availability of reactive sites for electrolytic ions and shortens the distance they need to travel, resulting in improved diffusion rates and enhanced electrochemical performance [10,12]. Energy-dispersive X-ray spectroscopy (EDS) was employed to analyze the distribution of tungsten (W), nickel (Ni), and oxygen (O) in the W–Ni films, as depicted in Figure S1a–c. The discernible peaks in the EDS spectra were assigned to the respective elements that exist in the film, providing additional confirmation of the W–Ni formation. Figure S1a–c presents detailed atomic percentage values, illustrating variations with different Ni doping concentrations.

The surface topography of the W–Ni samples was studied by atomic force microscopy (AFM) analysis, shown in Figure 6 (a) WNi-1%, (b) WNi-3%, and (c) WNi-5%. The 2-D AFM images of the samples revealed the formation of the nanogranules' surface structure with different developments. The AFM images of the 1% Ni-doped WO_3 sample (Figure 6a) depict small nanogranules with a tightly clustered morphology. In contrast, the AFM images of the WNi-3% sample (Figure 6b) reveal interconnected nanogranules with a well-defined porous structure. The nanogranules appear to have a more uniform arrangement compared to the 1% Ni-doped sample, suggesting a definite level of distribution. The presence of a well-defined porous structure indicates that the addition of 3% Ni dopant promotes the formation of nanogranules with enhanced surface area and porosity. The AFM images of the 5% Ni-doped WO_3 sample (Figure 6c) show nanogranules forming a compact surface. Unlike the other samples, the nanogranules in this sample exhibit a more compact and densely packed arrangement. As the crucial surface feature of the samples, the root mean square (RMS) roughness (R_q) values were approximately 9 nm, 14.7 nm, and 7.6 nm for WNi-1%, WNi-3%, and WNi-5%, respectively. The results demonstrated that the surface roughness is high for WNi-3%; this can be attributed to the interconnected well-grown surface structure facilitating the rougher surface.

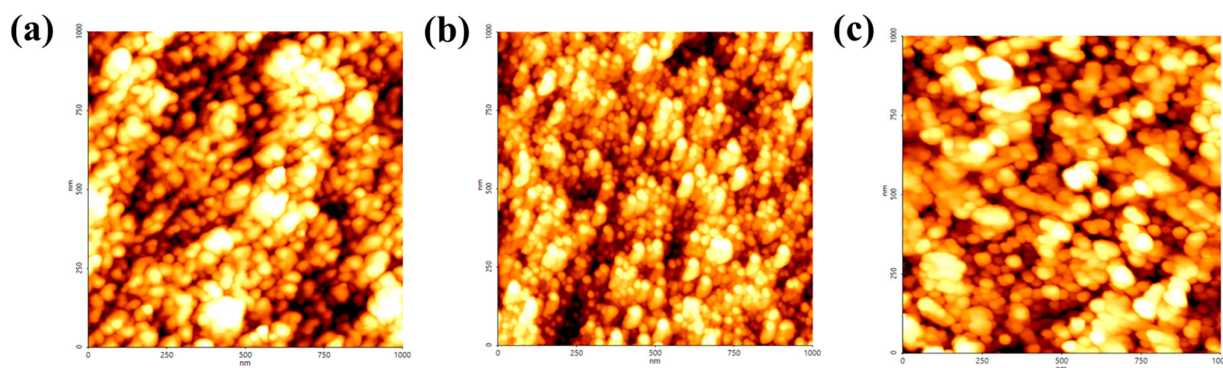


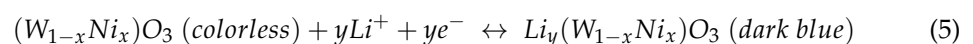
Figure 6. AFM images of W–Ni thin films (a) WNi-1%, (b) WNi-3%, and (c) WNi-5%.

Transmission electron microscopy (TEM) was performed to obtain the detailed morphology and surface structure. As shown in Figure S2a,b, it is clearly viewed that WNi-3% is an organized nanogranule morphology. Additionally, the elemental mapping (Figure S2c–e)

was conducted on the WNi-3% sample, allowing for precise elemental characterization and mapping of W, Ni, and O within the material. The images reveal that all the elements are distributed meticulously. This confirms that the Ni element successfully doped the WO₃ matrix.

5. Electrochromic Analysis

A thorough evaluation of W-Ni electrode CV profiles was conducted, employing a three-electrode electrochemical configuration. Experimental measurements were meticulously executed over an operational potential range of +1 to −1 V vs. Ag/AgCl, utilizing a 1M LiClO₄ + PC aqueous electrolyte. The CVs of W-Ni thin films were systematically recorded across varying scan rates (10 to 100 mV/s) and are illustrated in Figure 7a–c for in-depth analysis. The CV profiles exhibit a nearly homogeneous nature, characterized by well-defined and broad redox peaks, indicative of notable electrochemical behavior and reversibility. A discernible linear correlation is noted between the enclosed area within the CV and the sweep rate. This occurrence is ascribed to the elevated potential scan rates, leading to the shortening of the diffusion path at the electrode surface, thereby augmenting the current density [12]. The WNi-3% electrode demonstrated a significantly elevated redox peak current accompanied by a maximal area under the CV, substantiating the superior electrochemical performance of WNi-3% relative to WNi-1% and WNi-5%. The interconnected porous nanogranules forming a homogeneous network in the WNi-3% electrode facilitate abundant reactive sites, assisting facile charge diffusion. In contrast, electrodes WNi-1% and WNi-5% exhibit a diminution in peak currents in their respective CVs. This behavior is attributed to the compact and agglomerated surface structure, leading to a reduction in chemical reactivity for these samples [9]. The correlation between color switching and the redox behavior of the material elucidates that during a cathodic scan, the insertion of Li⁺ ions and electrons into the W-Ni host induces a color transition to a deep blue color. Conversely, the reverse process restores the electrode to its initial transparent state. The reduction (coloration) and oxidation (bleaching) behavior of the electrodes explicate the electrochromic effect, with the subsequent redox reaction presented as follows [10]:



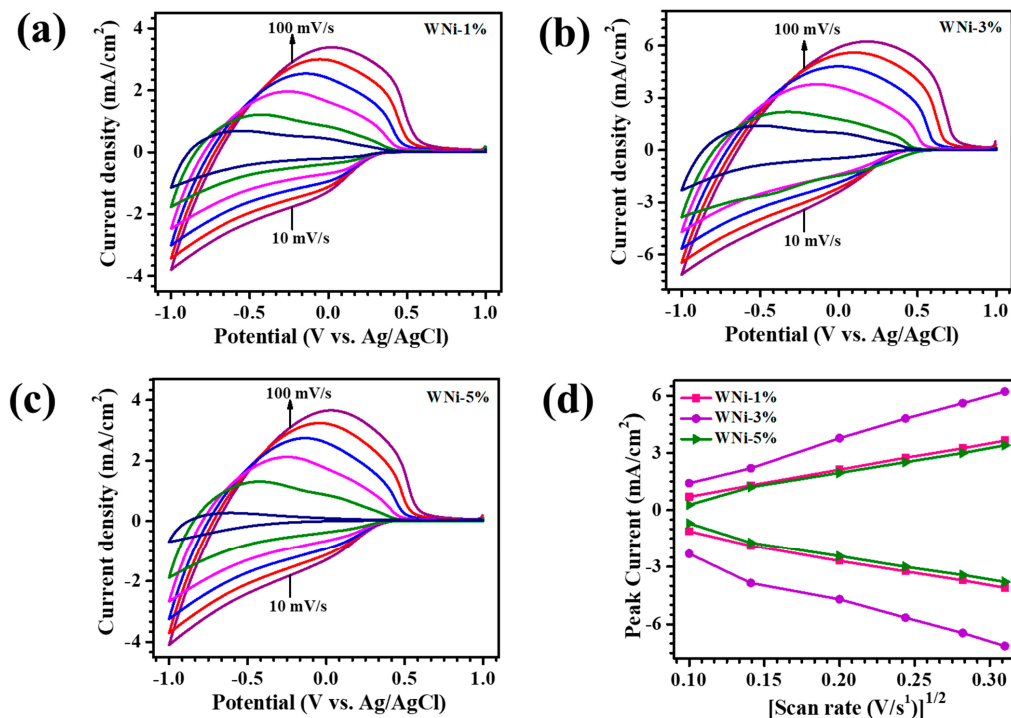
Subsequently, an intricate investigation into the charge transfer mechanism was undertaken based on the CVs to elucidate the current response mechanism. The plot of peak current density (i_p) against the square root of scan rate ($\vartheta^{\frac{1}{2}}$) is depicted in Figure 7d, providing insights into the analogous correlation between peak current and sweep rate. The determination of the diffusion coefficient of Li⁺ ions was accomplished using the Randles–Sevcik equation with i_p and $\vartheta^{\frac{1}{2}}$, conducted at a scan rate of 10 mV/s [9]:

$$D^{\frac{1}{2}} = \frac{i_p}{2.69 \times 10^5 \times n^{\frac{3}{2}} \times A \times C \times \vartheta^{\frac{1}{2}}} \quad (6)$$

In the equation, where i_p signifies the peak current, n represents the assumed number of electrons involved in the redox reaction, A denotes the area of the working electrode (cm²), C signifies the concentration of the electrolyte, ϑ stands for the scan rate, and D is the diffusion coefficient (cm²/s). The resultant cathodic and anodic diffusion coefficient values for N-W electrodes are specified in Table 1. It prominently illustrates a higher diffusion coefficient for WNi-3% (cathodic 1.86×10^{-9} cm²/s and anodic 0.7×10^{-9} cm²/s) compared to the other reference electrodes. These observations can further confirm that the electrochromic performance of WO₃ can be improved by the incorporation of an optimal quantity (3%) of Ni.

Table 1. Calculated Diffusion coefficient and evaluation of electrochromic measurements of WNi-1%, WNi-3%, and WNi-5% samples.

Sample Code	Diffusion Coefficient ($\text{cm}^2/\text{s} \times 10^{-9}$)		Q_i (C/cm^2)	Q_{di} (C/cm^2)	Reversibility	t_c (s)	t_b (s)	T_b (%)	T_c (%)	$\Delta T_{600\text{nm}}$ (%)	ΔOD	Coloration Efficiency (cm^2/C)
	Reduction	Oxidation										
WNi-1%	0.44	0.16	0.54	0.53	98.1%	13	6.5	94.2	22.4	71.8	1.436	53.18
WNi-3%	1.86	0.7	0.573	0.57	99.4%	12.4	10.2	92.8	10.9	81.9	2.141	75.12
WNi-5%	0.17	0.025	0.9	0.86	95.5%	14.5	9.6	86.3	34	52.3	0.100	22.22

**Figure 7.** Cyclic voltammetry of (a) WNi-1%, (b) WNi-3% (c) WNi-5% thin films at different scan rates (10–100 mV/s), and (d) Plot of peak current vs. (scan rate)^{1/2} of all samples for the diffusion coefficient.

Quantitative evaluation of the Li^+ intercalation/deintercalation dynamics from the N-W electrodes over time was achieved by chronocoulometry (CC) analysis. Figure 8a–c illustrates the CC plots for WNi-1%, WNi-3%, and WNi-5%, respectively, conducted in a 1M LiClO_4 + PC electrolyte. Cathodic polarization involves the introduction of charges into the material, leading to the reduction of W^{6+} to W^{5+} and the consequent transition of the film to a colored state. Next, the reverse potential induces the deintercalation of electrolytic ions, resulting in the oxidation of the host material back to W^{6+} . The reversibility of an electrochromic material is a pivotal parameter, influenced by the ratio of charges deintercalated (Q_{di}) to the number of charges intercalated (Q_i), expressed as follows [12]:

$$\text{Reversibility} = \frac{Q_{di}}{Q_i} \quad (7)$$

The obtained values of Q_i and Q_{di} , together with their calculated reversibility percentage are given in Table 1. The WNi-3% electrode demonstrated remarkable electrochromic performance, with a high reversibility of 99.4%. The favorable surface morphology of the WNi-3% electrode greatly improves its electrochromic characteristics. However, the WNi-1% and WNi-5% electrodes exhibited lower reversibility, indicating their inability to completely restore their initial state during the reverse bleaching process.

The investigation of doping's effect on the electrochromic performance of W-Ni thin films is elucidated through in situ transmittance spectra acquired in both colored and bleached states. The study encompasses various Ni doping concentrations (W-Ni-1%, W-Ni-3%, and W-Ni-5%) in WO_3 thin films, allowing for a comprehensive comparative analysis. Figure 9a shows the in situ transmittance spectra of the electrodes, captured within the wavelength range of 300 to 1100 nm under a potential bias of ± 1 V, with the corresponding transmittance outcomes briefly presented in Table 1. The thin films exhibit pronounced transparency in their bleached state, undergoing a transition to a colored mode when the -1 V was applied. The insertion of ions and electrons induces polaron absorption, serving as the underlying mechanism for the observed coloration in the visible optical spectrum of the thin films. Table 1 reveals that W-Ni-3% has an exceptionally high optical modulation (ΔT) of 81.9% at a wavelength of 600 nm, with 92.8% representing the bleached state (T_b) and 10.9% representing the colored state (T_c). This value is much greater than the optical modulations of W-Ni-1% ($\Delta T = 71.8\%$) and W-Ni-5% ($\Delta T = 52.3\%$). Figure 9b displays the digital photographs of a $4 \times 3 \text{ cm}^2$ EC device for W-Ni-3% sample in both its colored and bleached states. These images effectively showcase the film's capability to undergo color changes. The surface morphology of W-Ni-3%, characterized by interconnected nanogranules with a large surface area, imparts an excess of active sites conducive to Li^+ ion diffusion. This enhances the electrode–electrolyte interaction, which in turn improves both the coloration and bleaching processes. Notably, the nanogranules exhibit advantageous attributes, particularly their short ion diffusion length, contributing to a substantial ΔT [6,7,12]. Conversely, W-Ni-1% and W-Ni-5% thin films, characterized by surface denseness and nanogranule agglomeration, may impede the pathway for Li^+ ion intercalation and deintercalation, consequently resulting in a reduction in the ΔT .

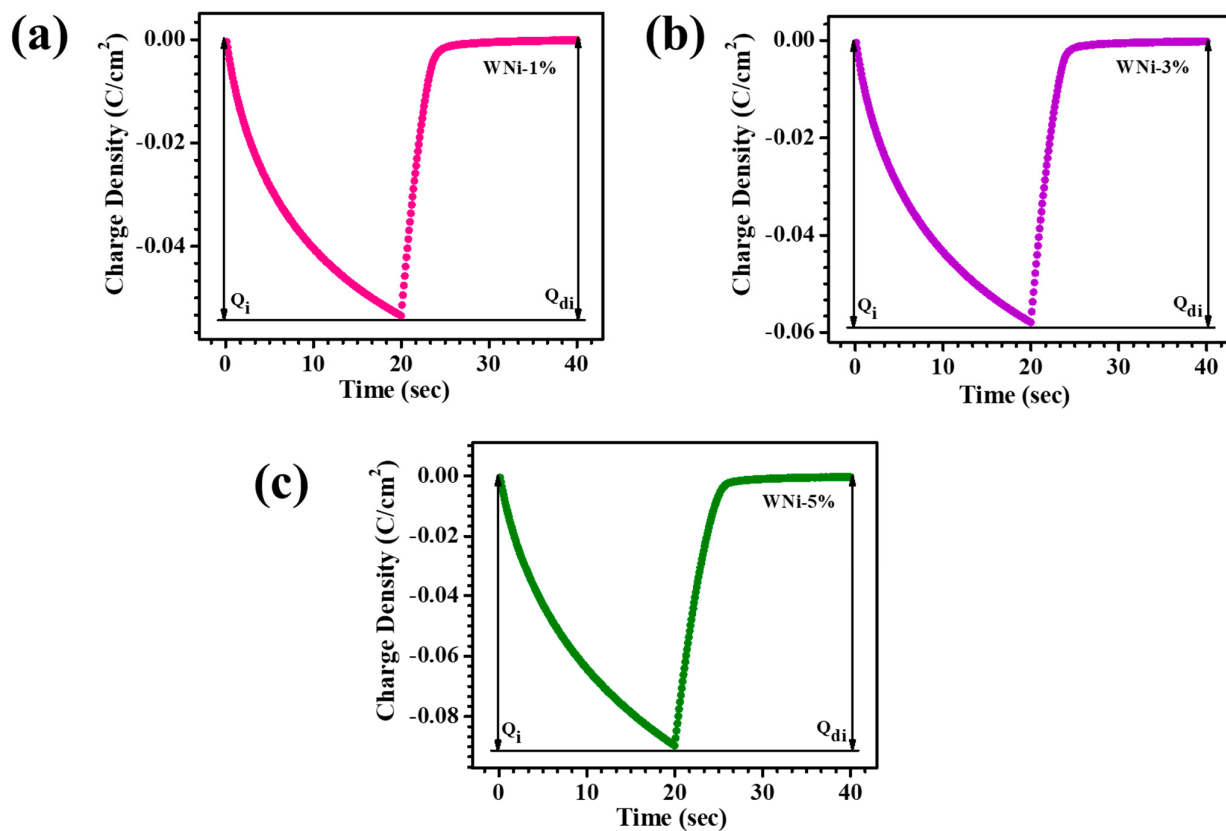


Figure 8. Chronocoulometry (CC) trace of W-Ni thin films at different concentrations (a) W-Ni-1%, (b) W-Ni-3%, and (c) W-Ni-5% thin films.

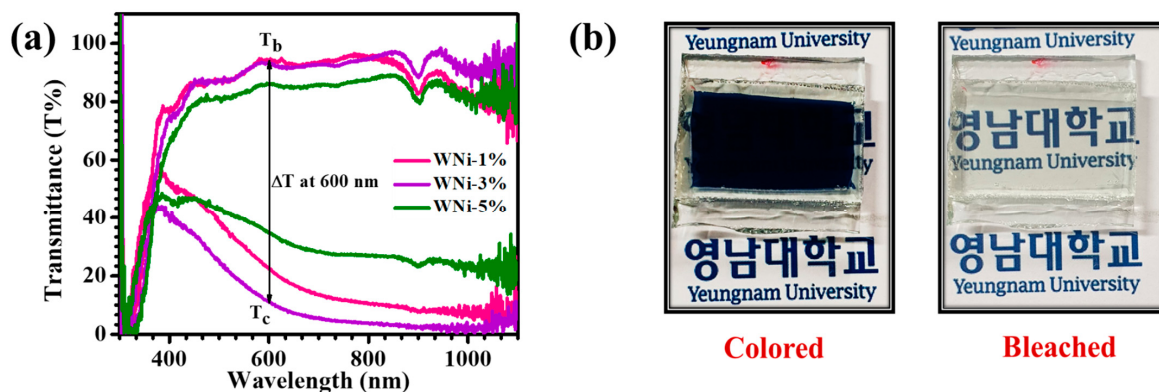


Figure 9. Combined optical transmittance spectrum of (a) WNi-1%, WNi-3%, and WNi-5% thin films at the colored and bleached states from 300 to 1100 nm range over potential window ± 1 vs. Ag/AgCl and (b) digital photographs of a 4×3 cm² EC device for WNi-3% sample in both its colored and bleached states.

The coloration efficiency (CE) is a crucial metric for evaluating the effectiveness of electrochromic materials. It is calculated as the as the variation in optical density (ΔOD) per unit of charge injected in the EC film at a given wavelength. The following equation is used to determine the coloration efficiency, which is proportional to the higher optical modulation of the film at a given charge density [9]

$$CE = \frac{\Delta OD}{(Q_{i/A})} \quad (8)$$

The amount of charge inserted per unit of electrode working area, denoted the $Q_{i/A}$, can be determined using the CC plot. The charge-dependent function corresponds to the quantity of charge in the sample, influencing the resulting ΔOD , as calculated through the given equation [12]

$$\Delta OD = \ln \frac{T_b}{T_c} \quad (9)$$

The bleached and colored states' transmittance values at the given wavelength (nm) are represented by T_b and T_c , respectively. Using the previously mentioned formula, the ΔOD and CE values for W-Ni thin films were computed in Table 1. The calculations for coloration efficiency indicated that the WNi-3% sample exhibited an enhanced CE value amongst all doped-WO₃ thin films, specifically 75.12 cm²/C at 600 nm. This enhancement in coloring efficiency suggests the potential to increase reaction kinetics and energy storage by incorporating metal ions with lower oxidizing capabilities than the host materials [20,22].

The notable optical modulation and high CE value are likely attributed to the interconnection of nanogranules, providing an enormous surface area for charge diffusion processes. A higher CE implies that a smaller amount of charge is needed to bring about a substantial change in transmittance. Conversely, the lower CE noticed for the other W-Ni samples (WNi-1% and WNi-5%) can be elucidated by the elevated charge insertion needed for the coloration process, resulting in minimal variations in ΔOD [23].

The coloration and bleaching time of electrochromic films are pivotal parameters that directly influence their performance and practical applicability. The coloration time represents the duration required for the electrochromic material to achieve its colored state, while the bleaching time denotes the time taken for the material to return to its initial, transparent state. Optimizing coloration and bleaching times is crucial for enhancing the real-world usability of electrochromic films in applications ranging from smart windows to display technologies, ensuring timely and efficient modulation of optical properties for desired functionalities. Herein, Figure 10a–c displays the optical switching analysis with the help of an in situ transmittance cycle together with a CA graph. The switching time

(described as the time required to achieve 95% of the optical contrast) and the calculated coloration time (t_c) and bleaching time (t_b) for W-Ni thin films are listed in Table 1. The WNi-3% electrode had a shorter coloring time of 12.4 s compared to the other electrodes. Bleaching time exhibited a significantly longer duration. Overall, the WNi-3% electrode has exceptional electrochromic performance in all aspects and is well suited for practical use.

In the realm of smart windows, the durability of electrochromic cycling stability is very important. The investigation of the EC characteristic retention capacity of thin films, namely WNi-1%, WNi-3%, and WNi-5%, was conducted using a UV-Vis spectrometer coupled with an EC cyclic tester in a standard three-electrode setup. The in situ transmittance cycles at 600 nm and the cyclic stability of current density (CA) were measured. Figure 11a–c illustrates the W-Ni thin films, and a combined plot of current density and optical stability was observed for each 40 s cycle at 600 nm, transitioning between colored (at -1 V) and bleached (at 1 V) states over 2000 s. During the coloration/bleaching cycle testing, the WNi-3% film demonstrated remarkable stability throughout the entire 2000 s, experiencing only a 4.6% deterioration in ΔT . This enduring performance is attributed to the porous surface morphology, providing structural stability, fewer ion trapping sites, and strong adherence to the substrate. In contrast, both WNi-1% and WNi-5% exhibited optical degradation of 11% and 23.3%, respectively, after the 2000s of electrochromic cycling. The T_b of W-Ni thin films exhibited a gradual decrease, while the T_c of all films remained generally steady. The decline in WNi-1% and WNi-5% thin films may be ascribed to significant ion trapping limiting the availability of active sites for ion adsorption and desorption, thereby contributing to the loss of transmittance [9,12,25].

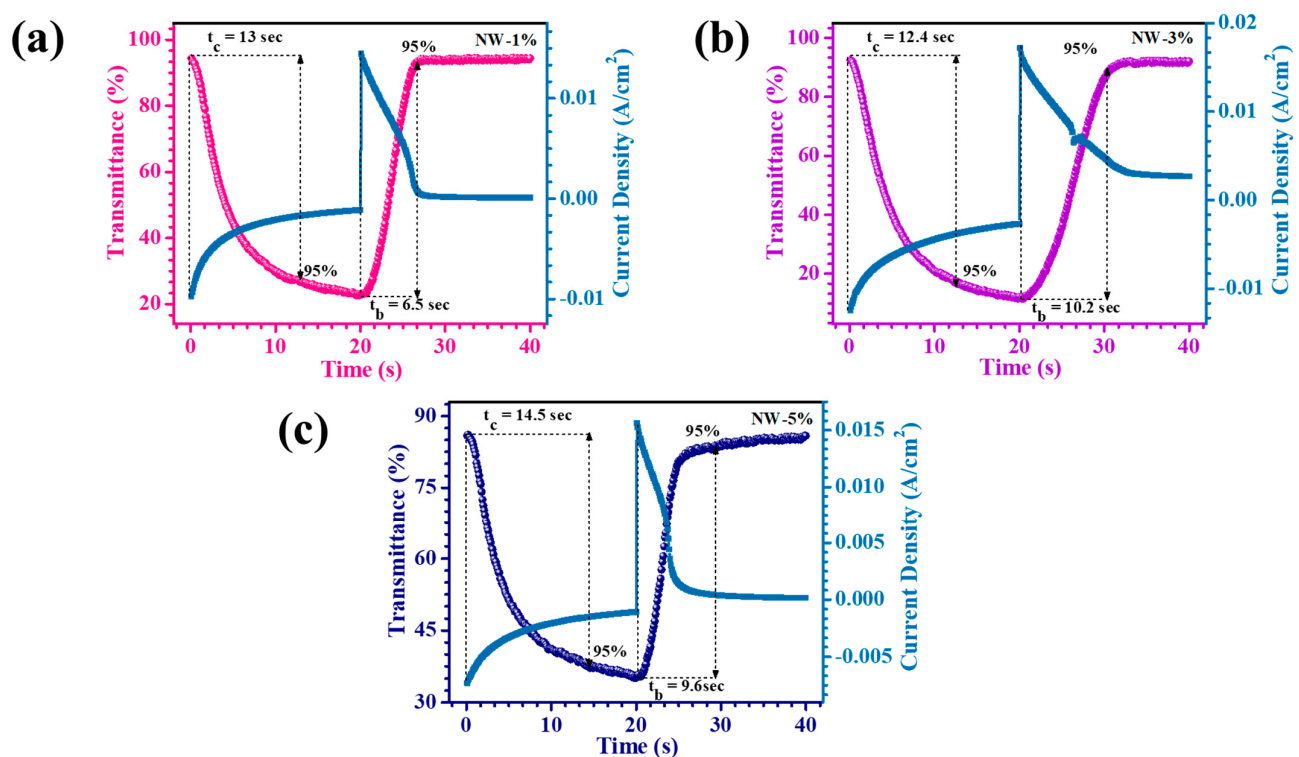


Figure 10. Chronoamperometric response time with in situ transmittance measurements of (a) WNi-1%, (b) WNi-3%, and (c) WNi-5% thin films in the colored and bleached state for 40 s.

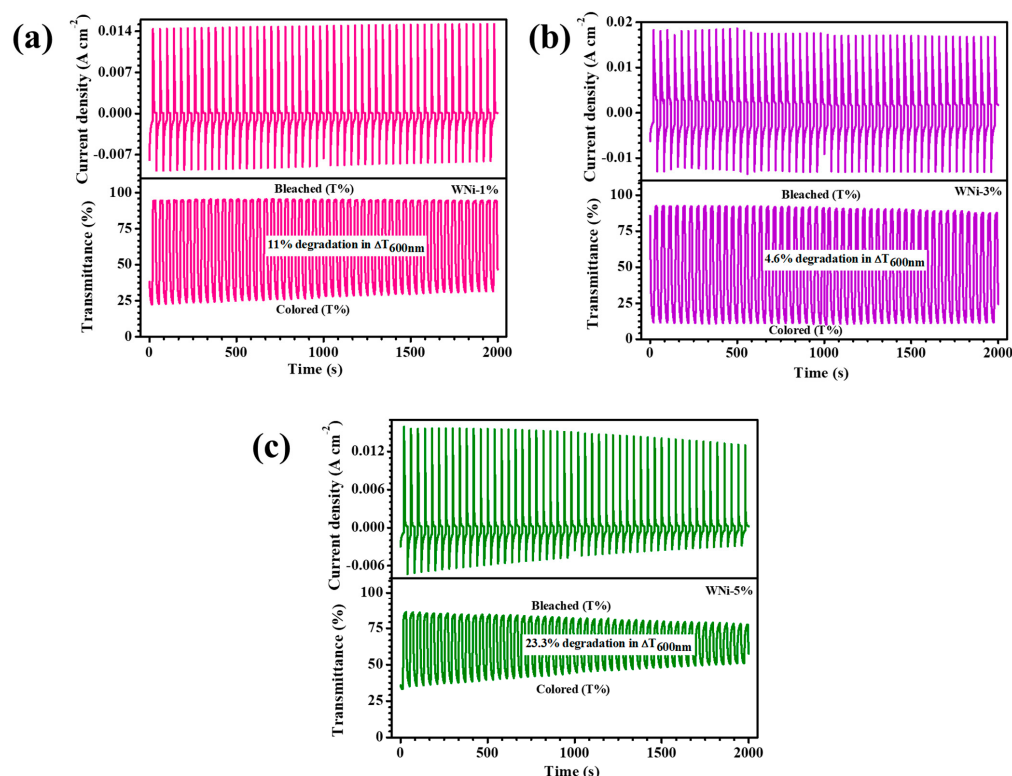


Figure 11. Plot of the long-term chronoamperometry curves with in-situ Optical response as a function of time of (a) WNi-1%, (b) WNi-3%, and (c) WNi-5%, thin films measured for 2000 s.

Our study focused on Ni-doped WO_3 by systematically investigating the effect of different Ni-doping concentrations on the structural, morphological, and electrochromic properties of the resulting electrodes. Specifically, we observed that the 3% Ni-doped WO_3 electrode exhibits superior electrochromic activity and stability compared to the 1% and 5% Ni-doped counterparts. This finding is novel and contributes to a deeper understanding of the optimal doping concentration for enhancing the performance of WO_3 -based electrodes. In the last several years, researchers have successfully synthesized and examined pristine and doped/composite WO_3 thin films and studied their electrochromic applications. Numerous studies extensively exploring the electrochromic properties of these materials have been published. However, there remains a lack of advancement in the realm of electrochromic technology. In this overview, Table S1 presents some data compiled from different sources that are focused on WO_3 electrochromic applications [24,41–45]. Different methods were used in preparing these thin films including hydrothermal, sol-gel, spin-coating, etc., which resulted in different surface morphologies including nanorods, nanosheets, agglomerated nanoparticles, and one with a compact surface. Comparing these results, it becomes evident that the WNi-3% electrode stands out, showing superior electrochromic characteristics. The simple and cost-effective electrodeposition technique that we utilized led to better control and facile synthesis of Ni-doped WO_3 that allows clearer understanding of the optimal doping concentration effect. The significance of our work extends to fundamental studies, as the optimized Ni-doped WO_3 electrodes hold promise for various electrochemical practical applications. By elucidating the relationship between Ni doping concentration and electrode performance, our study paves the way for the development of more efficient and sustainable energy-efficiency technologies.

6. Conclusions

This study details the effective synthesis of Ni-doped WO_3 (W-Ni) electrodes on FTO glass using a low-cost electrodeposition approach for electrochromic application, which is a widely industry-preferred technique. The produced W-Ni thin films had an

amorphous structure and nanogranular morphology, indicating promising possibilities for the cost-effective and scalable production of EC devices. Raman spectroscopy was used to analyze the WNi-3% thin film in both its colored and bleached phases. The investigation revealed important information about the development of redox tungsten and nickel species, highlighting alterations in valence states caused by reduction potential.

The electrochromic device constructed using the WNi-3% sample demonstrated superior electrochromic properties compared to other formulations (WNi-1% and WNi-5%). The optimized WNi-3% electrode displayed exceptional electrochromic performance, attaining the highest optical modulation (81.90%), outstanding reversibility (99.4%), and remarkable coloring efficiency (75.12 cm²/C). This enhanced performance of the W-Ni thin films was attributed to the substantial active surface area and abundant grain boundaries, effectively reducing the diffusion pathway and facilitating efficient electrolyte access into the film structure. These findings underscore the potential of the WNi-3% electrode for advancing electrochromic technologies, emphasizing its promising attributes for practical applications in cost-effective and scalable manufacturing processes.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/coatings14030320/s1>, Figure S1: EDS spectra and mapping analysis image of the WNi-1%, WNi-3%, and WNi-5% thin films. Figure S2: Transmission electron microscopy images of WNi-3% thin film at (a) 200 nm and (b) 50 nm, EDS elemental mapping of (c) W, (d) Ni, (e) O. Table S1: Comparative parameters of electrodeposited Ni doped WO₃ films with the reported literature and present work of electrochromic performance.

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