

Ultra-fast switching of energy efficient electrochromic nickel oxide thin films for smart window applications

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ABSTRACT

In today's modern world, energy consumption continues to escalate. In such cases, smart windows play a crucial role in reducing energy consumption and enhancing the quality of life. Electrochromic devices (ECDs) -based smart windows rely profoundly on nickel oxide (NiO) thin films, which act as a counter electrode in ECDs. This work aims to fabricate NiO thin films, with the intention of achieving ultrafast ECD. Through the sputtering technique, energy-efficient ECD is obtained with the highest optical modulation of 60 % at a rapid switching speed of 0.55s for bleaching and 0.95s for coloration. We have also investigated the structural, morphological, vibrational, and optical properties of NiO thin films. XRD analysis revealed the less crystalline or near amorphous nature of NiO thin film. XPS, PL, and Raman studies confirm the existence of defects in the film. The favourable, less crystalline nature, along with the presence of defects, facilitates ultra-fast ion intercalation and de-intercalation process. We believe that prepared NiO film can be used as a promising anodic colourant in electrochromic smart windows with applications in energy-efficient buildings.

1. Introduction

Electrochromism is a phenomenon by which the optical transmittance of a device may be changed from a colored state to a bleached one, and vice versa, by applying a regulated electric voltage. Over the last several decades, electrochromic materials have gained worldwide recognition for their use in energy storage and energy conservation applications. These applications include energy-efficient construction materials [1], aircraft windows [2], anti-glare rear-view mirrors [3], and heat-insulating glass [4]. Specifically, in wealthy nations, energy-efficient buildings contribute to around 30 % of the overall energy use [5–8]. A large percentage of the energy used by buildings is dedicated to the process of transporting heat from the building's structure to the outside environment, particularly via windows and doors. Consequently, the need for smart windows, which regulate visibility and solar radiation transmission to decrease building energy use, is increasing. An electrochromic window is a kind of smart window technology [9]. The energy savings of a smart window are equal to the energy generated by a solar panel located in the exact same location as the

smart window [10].

Thin films of electrochromic materials are used in “smart windows” (electrochromic devices) to control solar heat and light and provide privacy [11]. Electrochromic devices are comprised of anodic and cathodic colouring materials in a five-layer structure. The electrolyte, electrochromic layer, and ion storage (complementary) layer are sandwiched between two transparent conducting layers [12]. Several transition metal oxides, such as tungsten oxide (WO₃), nickel oxide (NiO), zinc oxide (ZnO), vanadium oxide (V₂O₅), and copper oxides (CuO) have been reported to exhibit good electrochromic (EC) properties [13–17]. Among these oxides, WO₃ is a cathodic electrochromic material that exhibits a colouring state due to the injection of ions and charge-compensating electrons. NiO is an anodic electrochromic material (a complementary layer) that exhibits colouring state due to the extraction of ions and charge-supplemented electrons [12].

During the process of electrochromism, electrons are transferred through a transparent conductor electrode to the electrochromic layer, and ions are inserted into or extracted from the thin film layers [13]. Generally, the electrochromic device's performance is highly influenced

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by the electrochromic film inside the device. The electrochromic characteristics of the device can, however, be controlled by variations in the ion storage layer. By inserting ions with opposite charges into the electrochromic layer, the ion storage layer effectively balances the ion charge [14]. In other words, a high charge capacity ion storage layer will improve electrochemical performance [15]. Therefore, the ion storage layer plays an irresistible and effective role in improving the electrochromic device's performance.

It is important to consider a few specific characteristics while designing an ion storage layer. For example, (i) an appropriate absorption spectrum in colored phases; (ii) a high absorption rate with minimal charge insertion results in high coloration efficiency; (iii) a stable and fast response applicable to both coloration and bleaching; (iv) a power conception less than 2 V; and (v) a low self-bleaching speed at zero potential [16].

An electrochromic device's ion storage layer is commonly fabricated with the metal oxides NiO, ZnO, V_2O_5 , and CeO_2 ; these oxides are selected to optimise the device's stability under a wide range of operating conditions [17–21]. Among these inorganic materials, nickel oxide films are an outstanding candidate for electrochromic devices since they change from a highly transparent state to a brownish state upon oxidation, a complementary effect to the blue coloration of tungsten oxide (cathodic material) electrodes. As well, nickel oxide, owing to its high charge capacity, finds applications in solar cells, lithium-ion batteries (LIBs), and electrochromic devices [22–29]. Anodic electrochromic materials made of NiO have a high optical contrast, stable memory behaviour, low cost, and a suitable voltage range, which makes them one of the supreme candidates for large-scale commercialization [17,30,31]. Nowadays, the rate at which electrochromism occurs is limited by its slow switching speed, especially in inorganic electrochromic materials. The slow reaction kinetics of inorganic electrochromic films are responsible for their poor switching speed. Additionally, these problems, such as optical contrast and response speed, need to be resolved in order to use NiO [17]. Numerous research has investigated the influence of modifications in the surface morphology of NiO thin films on the performance of electrochromic devices [31–35]. In their study, Zhengxin Li et al. reported improved electrochromic properties in NiO films with tertiary hierarchical porous architectures [36]. According to Dahyun Choi et al. controlling the crystalline size of deposited thin films increased the electrochromic performance utilising the optimised microstructure of the NiO ion storage layer [37].

As a vacuum deposition method, magnetron sputtering, both direct current (DC) and radio frequency (RF) modes, is superior to pulsed laser deposition (PLD), sol-gel, and hydrothermal methods due to its rapid deposition rate and ease of chemical composition adjustment [38–40]. Firstly, it allows for easy control of deposition conditions, with excellent films adhering to different substrates. With this technique, people won't have to come into contact with very dangerous chemicals or breathe toxic gases, as the vacuum system eliminates direct contact with them. Besides, the method is capable of depositing even very high melting point materials. In addition, it enables the simultaneous production of multi-layer coatings on multiple targets under a reactive gas atmosphere at extremely low pressures [41]. So, it is possible to combine the properties of different films into a single structure, including dielectric, semiconductor, and conductor. NiO thin films are extensively deposited using nickel metal targets (reactive magnetron sputtering) or by radio frequency (RF) sputtering from ceramic nickel oxide targets (typical non-reactive magnetron sputtering) [42].

As mentioned earlier, ECD changes colour when charged ions intercalate or de-intercalate. It is usually preferable to use proton (H^+) or lithium (Li^+) ions for the intercalation process because of their small sizes, which aid in higher mobility and easier intercalation. An electrolyte based on proton ions has greater ionic conductivity, while lithium-ion based electrolytes provide greater stability, a wider electrochemical active window, and inadequate dissolution, partly owing to

the absence of O_2 and water formation [43]. Another possible electrolyte for electrochromic devices is potassium hydroxide (KOH) in an aqueous solution. Even so, numerous studies have shown that nickel oxide undergoes sudden phase shift, self-discharge, and exhibits poor stability when using KOH electrolyte [24,25]. Moreover, it was found by Green et al. that WO_3 films may be fully dissolved (destroyed) in a KOH electrolyte solution [44]. Therefore, KOH poses challenges when used as an electrolyte in ECDs. According to K.J. Patel et al., the tungsten oxide thin film, when intercalated with H^+ ions, exhibits higher CE (coulombic efficiency) compared to larger ions such as Na^+ and K^+ . This is due to the H^+ ions having a higher diffusion coefficient in the WO_3 thin films [45].

The aim of the present investigation is to fabricate a NiO counter electrode (ion storage layer) for ECD via RF sputtering with enhanced electrochromic performance. The prepared NiO films were subjected to electrochromic studies such as cyclic voltammetry, chronocoulometry, and chronoamperometry techniques using various electrolytes with different molarities. The electrochromic study is carried out with propionic acid (for intercalating H^+ ions) and lithium perchlorate in propylene carbonate ($LiClO_4$ -PC) (for intercalating Li^+ ions). Furthermore, we examined the optical modulation using UV-Vis-NIR spectrophotometers and discussed the results in detail. Moreover, the evaluated electrochemical parameters from the electrochromic measurements were discussed in detail. We also studied several material properties, including structural, morphological, vibrational, and optical properties. These acquired results revealed that the deposited film has excellent electrochromic features like good transmittance modulation, rapid switching speed (response time), and very high coloration efficiency with acceptable reliability.

2. Experimental study

With an ultrapure nickel oxide target, we have fabricated nickel oxide thin films on well-cleaned FTO substrates via RF magnetron sputtering. A schematic illustration of the fabrication process is shown in Fig. 1. As shown in Fig. 1(a), the NiO target was placed 6 cm away from the FTO substrates. Argon gas with an extremely high level of purity was pumped into the chamber, and the pressure within the chamber was kept constant at 5×10^{-3} mbar throughout the deposition process. As shown in Fig. 1(a and b), when a rf (radio frequency) power of 100 W is applied, the argon atoms get ionised (Ar^+) and collide with the NiO target (which is the cathode and has a negative potential). These primary Ar^+ ions undergo a sequence of elastic and inelastic collisions with NiO target atoms, resulting in the loss of energy. The target atoms that rebound generate further collisions in a cascade manner, as shown in Fig. 1(b). Eventually, the energy from primary ions might get transferred to the surface atoms, and these atoms would be ejected if it overcame the binding energy. During this mechanism, the emission of secondary electrons occurs simultaneously with the emission of NiO atoms. The emitted secondary electrons recombine with the Ar^+ ions and release photons. At this moment, we can observe the occurrence of plasma. Simultaneously, the ejected nickel oxide atoms will reach the substrate and get deposited as a thin film. Thin films of nickel oxide were fabricated at room temperature (RT). To remove contamination, the NiO target was pre sputtered for almost 10 min. As stated in our earlier studies [46,47], film thickness was detected via stylus profilometry using the Mitutoyo SJ-301. We used X-ray diffraction (XRD) with X'pert Pro PANalytical to study the structural property. AFM; Nano scope-E were used to explore the surface morphology. The micro-Raman study was done via STR- Raman spectroscopy. We studied the elemental composition of the deposited film using X-ray photoelectron spectroscopy (XPS; JEOL PS-9010 TR). The optical characterization was accessed by UV-Vis-NIR spectrophotometer using a JASCO-V-670 instrument. The photoluminescence study was carried out via a Varian Cary Eclipse fluorescence spectrophotometer. We performed electrochemical studies on NiO films using an electrochemical workstation scanning potentiostat/galvanostat (CH Instruments Inc., USA; Model: CHI604D). Three

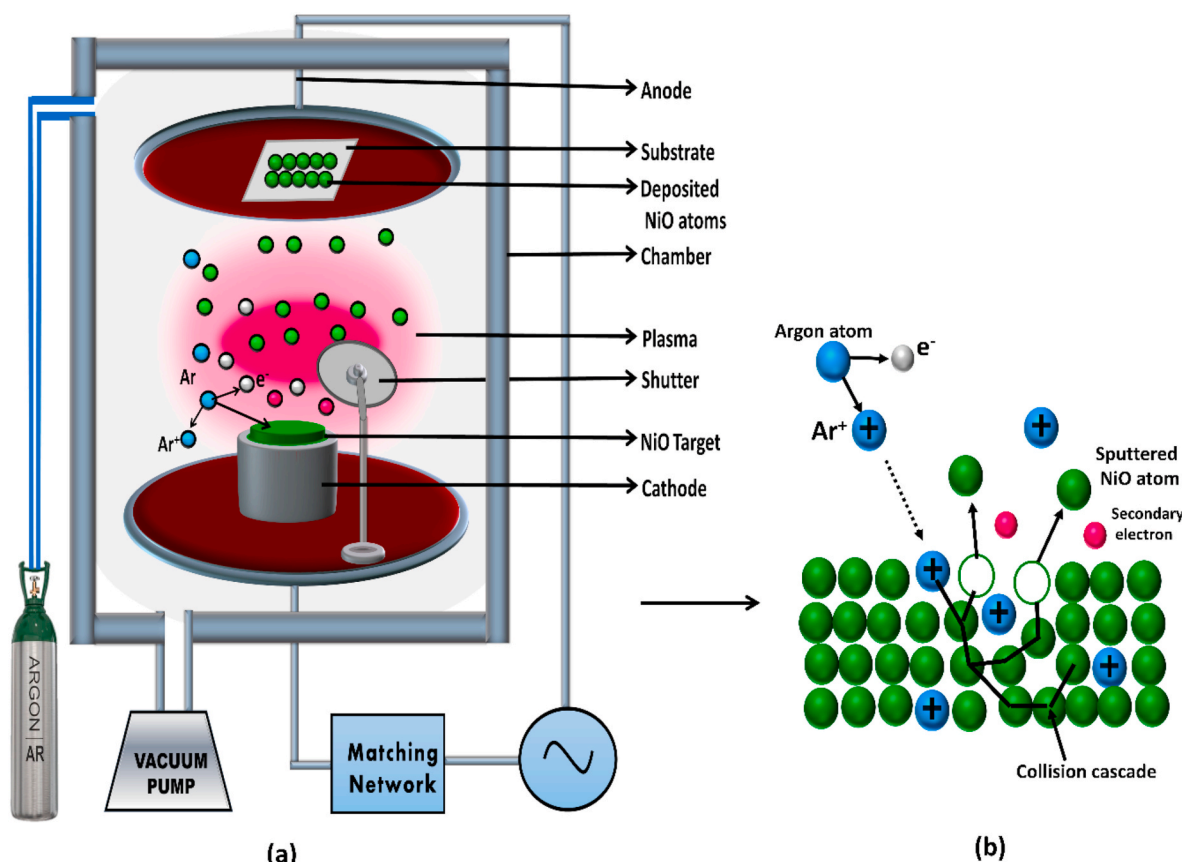


Fig. 1. (a). Schematic illustration of sputtering unit, (b) schematic illustration of sputtering process

electrode electrochemical cells were designed for the study: a working electrode (NiO films deposited on FTO substrates), a counter electrode (Pt mesh), and a reference electrode (Ag/AgCl). Propionic acid and lithium perchlorate in propylene carbonate (Li-PC) were used as electrolytes.

3. Results and discussion

3.1. Structural studies

The thickness of the nickel oxide thin film deposited on the FTO substrate was detected to be 0.73 μm . The X-ray diffraction pattern, depicted in Fig. 2 (a), reveals that the prepared NiO thin film had a cubic structure. The cubic crystal structure of the deposited NiO thin film (space group Fm-3m) is depicted in Fig. 2(b) using VESTA software. The diffraction peaks observed at 2θ values of 43.03° and 62.2° correspond to the (200) and (220) orientations, respectively. For a better understanding of the crystal structure of NiO, with (200) and (220) lattice planes were drawn and portrayed in Fig. 2(c). The perceived values matched well with the standard JCPDS Card No: 89–7130. Also, the observed broad and less intensity of NiO peaks indicate the less crystalline or near amorphous nature of the film. Modifications in the structure and morphology of nickel oxide can enhance its electrochromic performance. Arakaki et al. have reported that the EC performance of amorphous NiO films deposited at 220°C were better than those of cubic crystals at 400°C in 0.1 M KOH electrolyte [48]. Amorphous NiO films exhibits superior electrochromic performance compared to crystalline NiO films, specifically in terms of faster switching speed and higher optical modulation. This is due to the highly disordered structure of amorphous NiO films, which facilitates the rapid movement of electrolyte ions within the film and allows for a greater number of electrolyte ions to be accommodated [49,50]. Therefore, the

deposited, less crystalline or near amorphous NiO thin film can offer enough diffusion pathways for enhanced electrochromic performance [51]. The several structural parameters, like crystallite size (D), strain (ϵ), number of crystallites per unit area (N), and dislocation density (δ), retrieved from the (200) diffraction peak, were calculated and given in table 1 [52].

3.2. Surface morphological study

The electrochromic performance of a thin film is strongly dependent on its morphology. Atomic force microscopy (AFM) may be used to get a comprehensive examination of the inter-grain areas and individual grains of a material in a three-dimensional (3D) format. Furthermore, the AFM has the ability to analyse the characteristics of the surface. This information about NiO film may be used for electrochemical investigations. An NiO film was deposited onto a glass substrate at room temperature using a power of 100W. The film was then examined using AFM. The examination was conducted at several levels of magnification, and the AFM pictures are shown in Fig. 3. Fig. 3(a–d) depict the 2D and 3D micrographs of the films, showing their topographical features. The micrographs cover a surface area of $5 \times 5 \mu\text{m}$ and $2 \times 2 \mu\text{m}$, respectively. The deposited film has a homogeneous surface with a pin-hole free nature. The growth of tiny and isolated nuclei morphology was observed. Surface roughness has a major influence on the optical, electrical, and mechanical properties of films. Surface roughness is a crucial factor in understanding light scattering at the film surface. The minimum surface roughness of the film reduces light scattering, which can increase the optical transmission of the film [53]. The surface roughness (R_{rms}) value of 0.736 nm was acquired, which is less in comparison with the reported R_{rms} values for NiO films [11,54–56], which represents the smoothness of the surface.

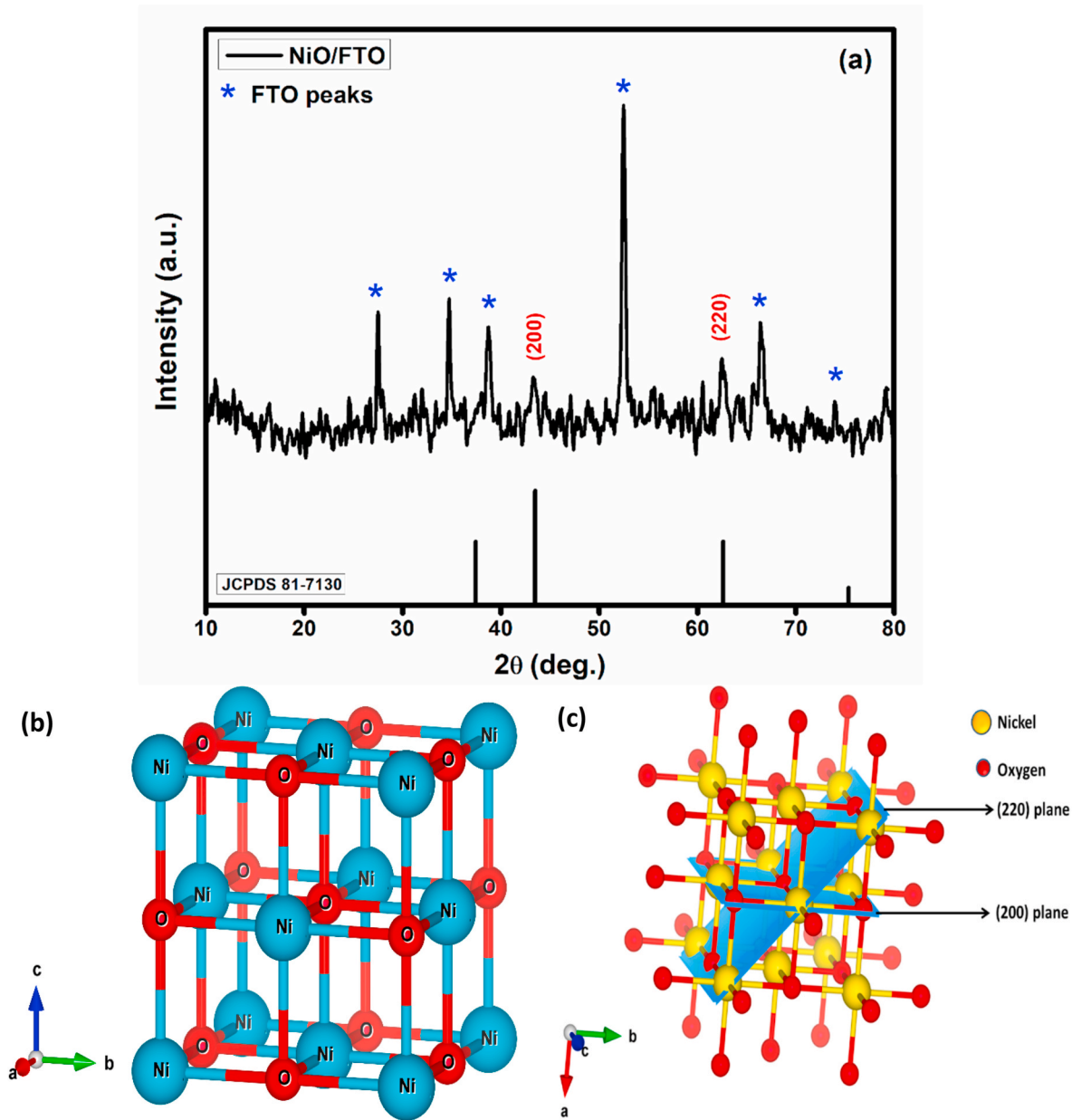


Fig. 2. (a) XRD spectra of NiO thin film, (b). Crystal structure of cubic NiO thin film drawn using Vesta software, (c) Crystal structure of cubic NiO thin film with (200) and (220) lattice planes drawn using Vesta software

Table 1
Structural parameters of NiO thin film prepared on FTO substrate.

2θ	FWHM	hkl	d-spacing (Å)	Lattice Constant (a) Å	Crystallite size (D) (nm)	Dislocation density (δ) × 10 ¹⁶ lines/m ²	Strain (ε) (lines ⁻² m ⁻⁴) × 10 ⁻³	Number of crystallites per unit area (N) × 10 ¹⁷ /m ²
43.08	0.6	200	2.09796	4.19592	5	4.2	7.4	74

3.3. Micro-Raman analysis

A Raman study could be performed to investigate the structure of NiO films and identify defects in the lattice. Fig. 4 depicts the micro-Raman spectra of NiO film prepared on an FTO substrate. As portrayed in Fig. 4, the sputtered NiO thin film shows two characteristic peaks at 560 cm⁻¹ and 1100 cm⁻¹. This endorses the formation of NiO films. The Raman band observed at 560 cm⁻¹ is imputed to a first-order longitudinal (LO) mode. The stronger second- order band located at

1100 cm⁻¹ represents the longitudinal (2LO) mode [57]. These first- and second- order LO modes are related to the vibrations of Ni–O bonds. Faycal Chandoul et al. reported peaks at 510 and 1087 cm⁻¹ which belong to the first-order (1p:TO and LO modes) and second-order (2p:2LO modes) phonon scattering, respectively, for NiO thin film [58]. Salunkhe, P. et al., indicated that Raman scattering was observed at 579 and 1119 cm⁻¹ for sputter coated NiO thin films [57]. Furthermore, first-order LO phonon scattering in NiO occurs because of nickel vacancy (defects) or the presence of Ni³⁺ ions [57]. This represents the

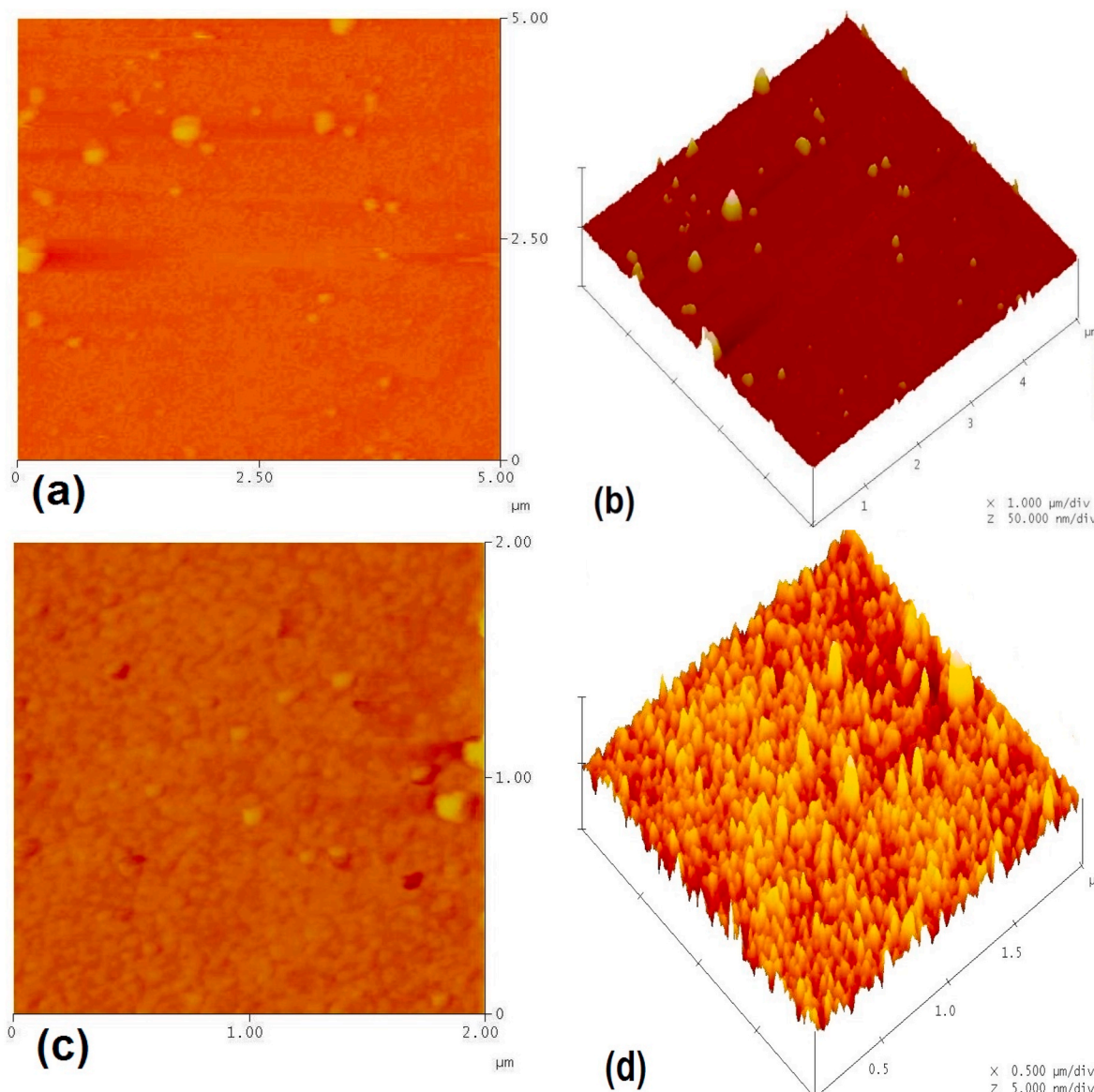


Fig. 3. AFM images of NiO thin film (a) 2D AFM image at 5 μm scan size, (b) 3D AFM image at 5 μm scan size, (c) 2D AFM image at 2 μm scan size, (d) 3D AFM image at 2 μm scan size.

existence of Ni_2O_3 in the deposited film. Also, the broad nature of the Raman peaks represents the less crystalline or near amorphous nature of NiO thin films [47]. This is consistent with our XRD results. The existence of defects can narrow the bandgap of the visible absorption of nickel oxide and enhance the ability of the H^+/Li^+ ion intercalation, which further enhances the electrochromic process [59].

3.4. Chemical analysis

An XPS survey scan has been performed for the NiO films deposited on glass substrates, and the same is displayed in Fig. 5. A characteristic peak for nickel (Ni) as well as for oxygen (O) has been detected in the current study, indicating that the prepared NiO films were pure and of good quality. The deconvoluted nickel ($\text{Ni}2\text{p}$) and oxygen ($\text{O}1\text{s}$) core level spectra for the films prepared at similar conditions are further shown in Fig. 5(b and c). Two strong peaks detected at 853.53 eV and 859.72 eV correspond to $\text{Ni}2\text{p}_{3/2}$. Moreover, two more peaks at 871.63 eV and 878.15 eV were detected, which are associated with $\text{Ni}2\text{p}_{1/2}$ levels. Further, we found a separation of 18.9 eV among $\text{Ni}2\text{p}_{3/2}$ and $\text{Ni}2\text{p}_{1/2}$, which is consistent with previous reports [60,61]. Another peak is

observed at 855.62 eV, which overlaps with Ni^{2+} (853.53 eV), indicating the existence of Ni^{3+} and Ni^{2+} [42]. According to oxygen core level spectra, the peak corresponding to $\text{O}1\text{s}$ was discovered at 529.31 eV. From the deconvoluted core level spectra of $\text{O}1\text{s}$, another peak associated with Ni^{3+} was discovered at around 531.12 eV. This confirms the co-existence of Ni_2O_3 along with NiO. Table 2 displays the binding energy (BE) values for Ni and O and the compositions of each. The detected BE values are in agreement with the literature [61]. Moreover, the presence of Ni^{3+} cations can contribute to the formation and diffusion of carriers, which facilitates the electrochromic mechanism [42].

3.5. Optical properties of NiO thin films

The film deposited on the FTO substrate had an average transmittance of 85 %, indicating the high quality of the film. Fig. 6 (a) illustrates the absorbance spectra of NiO thin films. According to the study, the absorption of light with wavelengths over 400 nm was caused by a high amount of oxygen in the lattice. This abundance was a consequence of either the creation of vacancies in the lattice or the presence of Ni^{3+} ions alongside Ni^{2+} ions in NiO films [62]. The

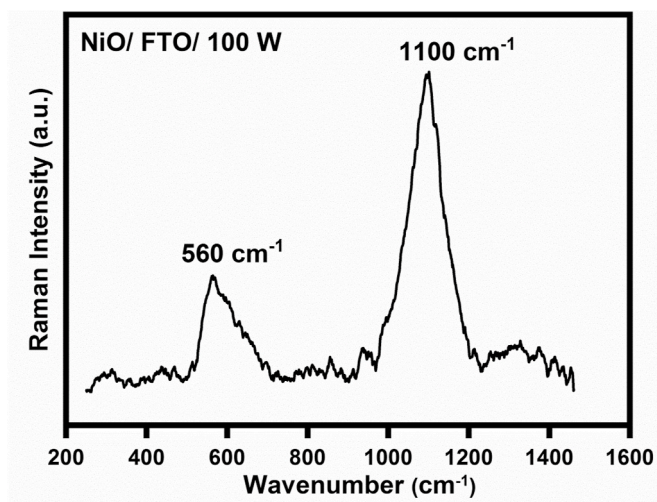


Fig. 4. Raman spectra of NiO thin films

measured absorbance of the deposited NiO film suggests the presence of both Ni^{3+} ions and Ni^{2+} ions in the film. This inference is in agreement with the XPS measurement. The ripple patterns observed in the visible region might be owing to the typical interference between the light photons and NiO films. This interference may be because of the homogeneous nature of the film on the substrate. This indicates that the fabricated NiO films are suitable for electrochromic applications.

The energy band gap (E_g) of the films was evaluated using the traditional Tauc plot, $(\alpha h\nu)^2$ versus $h\nu$, as shown in Fig. 6 (b). Extrapolating the linear part of the curves Fig. 6 (b) to the energy axis (at $\alpha h\nu = 0$) results in the E_g of films. The energy bandgap E_g , Fig. 6 (b), is found to be 3.12 eV.

3.6. Room temperature photoluminescence study (RTPL) on NiO thin films

For measuring the RTPL spectra, the deposited NiO thin films were excited at a wavelength of 270 nm. As shown in Fig. 7, the RTPL emission spectra show two solid emission peaks detected at 365 nm (3.39 eV) and at 420 nm (2.95 eV). The major peak identified at 365 nm belongs to near-band-edge (NBE) emission, which occurred owing to the radiative recombination process [54]. The next blue emission peak detected at 420 nm might be ascribed to the exciton recombination

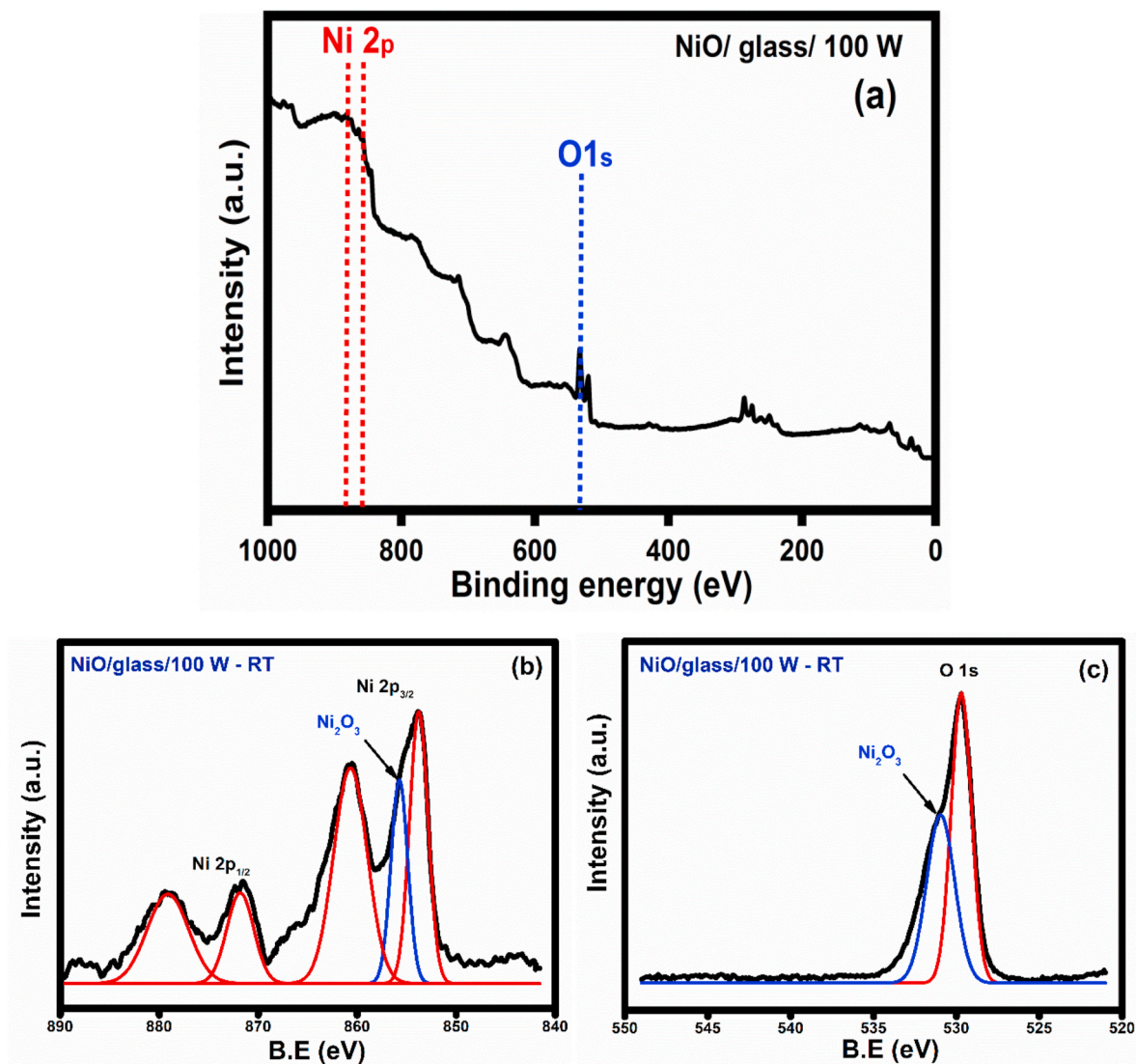


Fig. 5. (a) XPS survey scan spectra of NiO thin film, (b) XPS core level spectra of Ni, (c) XPS core level spectra of O.

Table 2

XPS core-level binding energy values of Ni and O for NiO thin film deposited on glass substrate.

Element	Atomic Concentration (%)	Binding energy (eV)						
		Ni 2p _{3/2}		Ni 2p _{1/2}			O 1s	
Ni	44.81	853.53	855.62	859.72	871.63	878.15	–	–
O	55.19	–	–	–	–	–	529.31	531.12

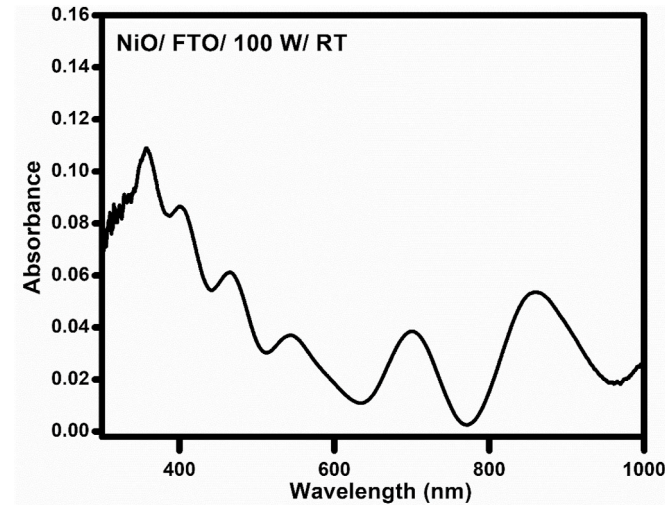


Fig. 6 (a). Absorbance spectra of NiO thin film

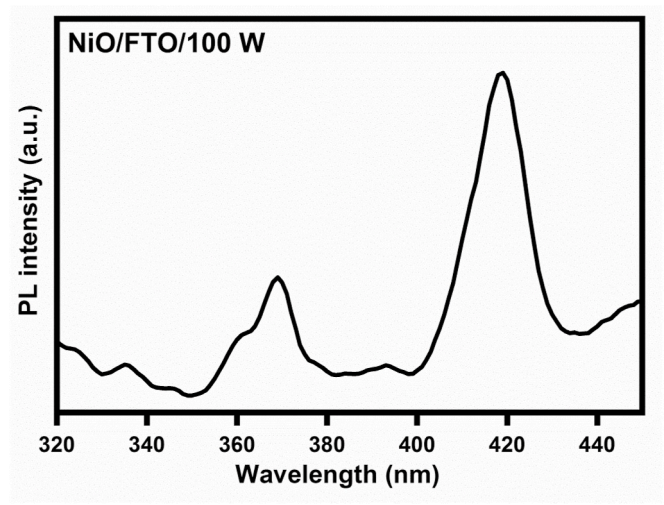


Fig. 7. Photoluminescence spectra of NiO thin film

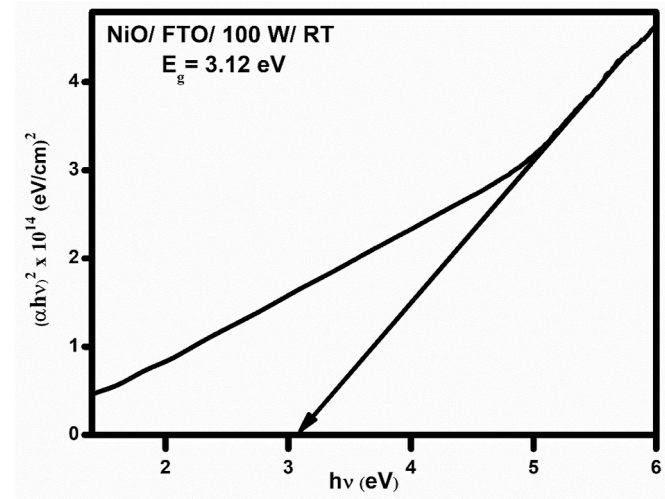


Fig. 6 (b). Tauc plot of NiO thin film

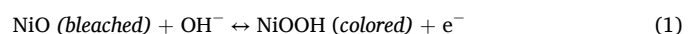
process (non-radiative transition) [58]. Generally, this exciton PL emission mostly arises from the vacancies, interstitials and defects present in semiconductors. Hence, the observed blue emission peak may be attributed to the existence of defects, which are induced by excess oxygen or nickel vacancies in the film. Fig. 7 clearly demonstrates that the strength of the visible emission peak (420 nm), which corresponds to defect level emission, is significantly greater than the UV emission peak (365 nm). This indicates the existence of nickel vacancies or an excess of oxygen in the NiO thin film. This is consistent with the existence of Ni³⁺ ions, as determined by Raman and XPS investigations. The presence of defects favours electrochromism.

3.7. Electrochemical analysis

We used cyclic voltammetry (CV), chronocoulometry (CC), and chronoamperometry (CA) to inspect the electrochromic behaviour of prepared NiO thin films over FTO substrates. The study was performed by fabricating three electrode electrochemical cells with a working electrode (NiO films on FTO substrates), a Pt mesh as a counter electrode, and an Ag/AgCl reference electrode. The analysis was done via the intercalation and de-intercalation of H⁺ and Li⁺ ions.

The switching of the bleached and colored states in the nickel oxide occurs due to the intercalation and deintercalation of ions, respectively. The electrochemical reaction scheme depends on the nature of the film and the electrolyte. Although the colouring process of tungsten oxide is well understood, the coloration mechanism of NiO remains unclear. A possible explanation for the complexity is the presence of many phases in both the bleached (α and β phases) and colored (γ and β phases) stages [63]. Studying the colouring process is further complicated by the potential occurrence of numerous reactions in an aqueous electrolyte during cycling. The coloration's responsible ions are a subject of contradictory results, with both H⁺ and OH[−] ions being identified as dominating. There have been lots of studies performed on nickel oxide in electrolytes such as protic and basic potassium hydroxide (KOH), protic and acidic propionic acid, and aprotic and Lewis acidic lithium perchlorate in propylene carbonate (Li-PC) [44].

As per the report [64], when using KOH as an electrolyte, during anodic scanning, NiO reacts with OH[−] ions present in the electrolyte, and the applied voltage pulls the electrons out of the film. This causes the coloration in the film. At this point, the film transforms into dark brown NiOOH. In the reverse process during the cathodic scan, the application of voltage causes the injection of electrons into the film, while the OH[−] ions return to the electrolyte. As a result, NiOOH is converted back into Ni(OH)₂, causing the dark brown colour to fade away and the film to become transparent. The electrochemical mechanism of NiO in KOH is given below.





Avendano et al. [65] showed that protons were the species responsible for (de)intercalation from KOH. The film is colored by the extraction of protons from the hydroxide phase; and the initial condition is restored by inserting the protons again. However, in the case of propionic acid and Li-PC, it appears that no ions can be extracted from the as-deposited NiO film. Instead, in propionic acid and Li-PC, on the other hand, it seems that no ions can be extracted from the as-deposited film itself, i.e., H^+ (from propionic acid) and Li^+ (from lithium perchlorate) inside the electrolyte are the ones responsible for the optical modulation [44]. Insertion of H^+ or Li^+ leads to the bleaching of the film, and the coloration is achieved by the extraction of the ions.

3.8. Intercalation/de-intercalation of H^+ ion

For proton (H^+) insertion and de-insertion on NiO films, propionic acid has been used as an electrolyte solution. A CV study was performed with propionic acid at 0.1 and 0.5 M. Against Ag/AgCl (with various scan rates of 25, 50, 100, and 150 mV/s), cyclic voltammograms were done with the linear potential sweep between -1.0 and 1.9 V. The CV curves for NiO thin films cycled in 0.1 M and 0.5 M propionic acid (PA) electrolyte solutions are shown in Fig. 8 (a & b). In NiO, the coloration or bleaching mechanism is achieved by the extraction/insertion of electrons from 3d bonds [66] without the metal-oxygen bond being disrupted. Nickel oxide's valence band is composed of nickel 3d states at the top, followed by an oxide 2p state at the bottom [67]. Colored states represent partially filled valence bands, or vacancy electrons (or nickels) on nickel atoms. The coloration and bleaching mechanisms of NiO can be written as:



An electrochromic device is shown in Fig. 9 (a). During the cathodic potential scan ranging from $+1.9$ to -1.0 V, the process of reducing Ni^{3+} to Ni^{2+} occurs. Through the application of an external electric field, both H^+ ions and electrons are directed towards the electrochromic NiO layer, as seen in Fig. 9 (b). This movement occurs across the propionic acid electrolyte. As the electrolyte does not conduct electrons, it drives the charge-balancing electrons to pass through an external circuit and then recombine with the ions within the material. Electrons flow quicker through electrochromic NiO, interacting with ions at the surface and diffusing into the material. This suggests that the electrochemical reaction occurs at the surface. Intercalation of H^+ ions create new localized energy states near the valence band. The supplied electrons fill vacant energy sites in the NiO thin film. As many more electrons are

inserted, they occupy the available energy states in a sequential manner, causing the Fermi level to shift towards higher energy levels. As a consequence of this alteration in the Fermi level, the electrical conductivity and optical characteristics were modulated, which ultimately led to the bleaching of the NiO semiconductor layers as shown in Fig. 9 (c). Fig. 9 (c) represents an electrochromic window in the bleached state, in which both visible and IR rays (light and heat rays) travel through the window completely. H^+ ion intercalation/deintercalation modifies the Fermi level, and this transforms the material between transparent and colored. In the reverse process Fig. 10 (a), upon de-intercalation of H^+ ions, as shown in Fig. 10 (b), Ni^{2+} ions are oxidised to Ni^{3+} during the anodic scan from -1.0 to $+1.9$ V. The Fermi level now moves down to the lower energy level, resulting in a brownish color of NiO film, as given in Fig. 10 (c). As depicted in Fig. 10 (c), upon de-intercalation, the window will turn to a brown colour, and both visible and IR rays (light and heat rays) can be partially blocked by the window.

We have calculated various electrochromic parameters from the cyclic voltammograms (calculated by equation (4)) in order to gain a better understanding of the electrochemical study of NiO films. These parameters include anodic peak currents (i_{pa}), cathodic peak currents (i_{pc}), and diffusion coefficients (D).

$$i_p = (2.69 \times 10^5) n^{3/2} A D^{1/2} \nu^{1/2} C \quad (4)$$

Peak current, number of electrons transferred, electrode area, diffusion coefficient, scan rate, and analyte concentration in bulk state are all represented by i_p , n , A , D , ν and C . The evaluated i_{pa} , i_{pc} , and D values for the films cycled in 0.1 M and 0.5 M propionic acid are tabulated in table 3. The D values obtained are similar to those reported in the literature [37,68,69]. Based on table 3 and it can be seen that anodic and cathodic peak currents increase with an increase in scan rate. At slow scans, diffusion layers grow farther from electrodes than at fast scans, resulting in much smaller fluxes to the electrode surfaces than in faster scans. Meanwhile, the current magnitude is proportional to the flux towards the electrode; a slow scan rate results in a lower current magnitude, and a high scan rate results in a high current magnitude. As a result, the higher scanning rate leads to more intercalation and de-intercalation of H^+ ions in NiO films.

Chronocoulometry (CC) is a technique used to quantify the number of protons or ions that either enter or exit a system during a potential double step. Fig. 11 (a) shows the colored and bleached states of films cycled in 0.1 and 0.5 M propionic acid solutions using a potential sweep of -1.0 to 1.9 V vs Ag/AgCl. Table 4 shows the estimated charge intercalated (Q_{in}) and de-intercalated (Q_{di}). The electrochromic reversibility can be obtained by using the following relation:

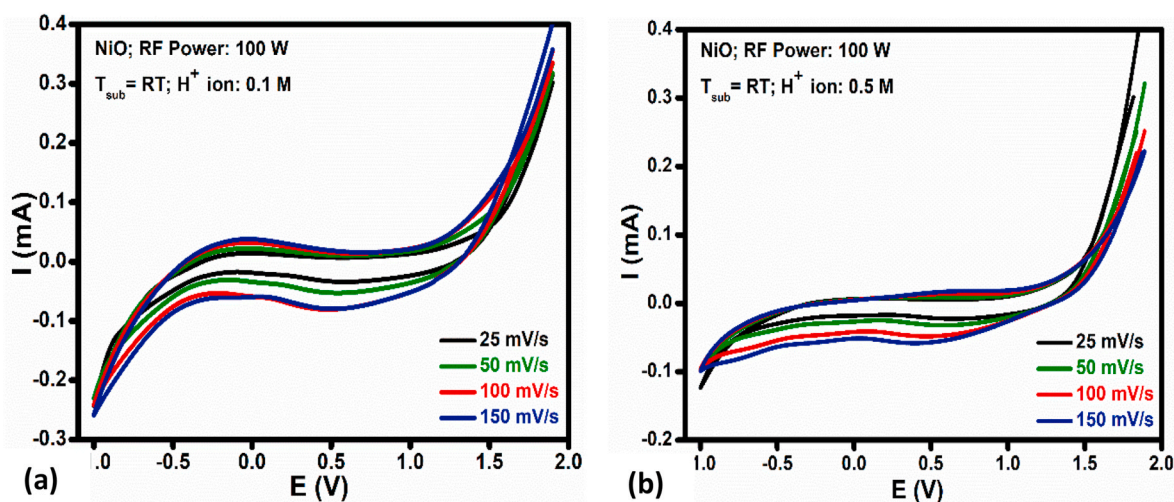


Fig. 8. (a) Cyclic voltammetry curves of NiO film cycled in 0.1 M PA, (b) Cyclic voltammetry curves of NiO film cycled in 0.5 M PA.

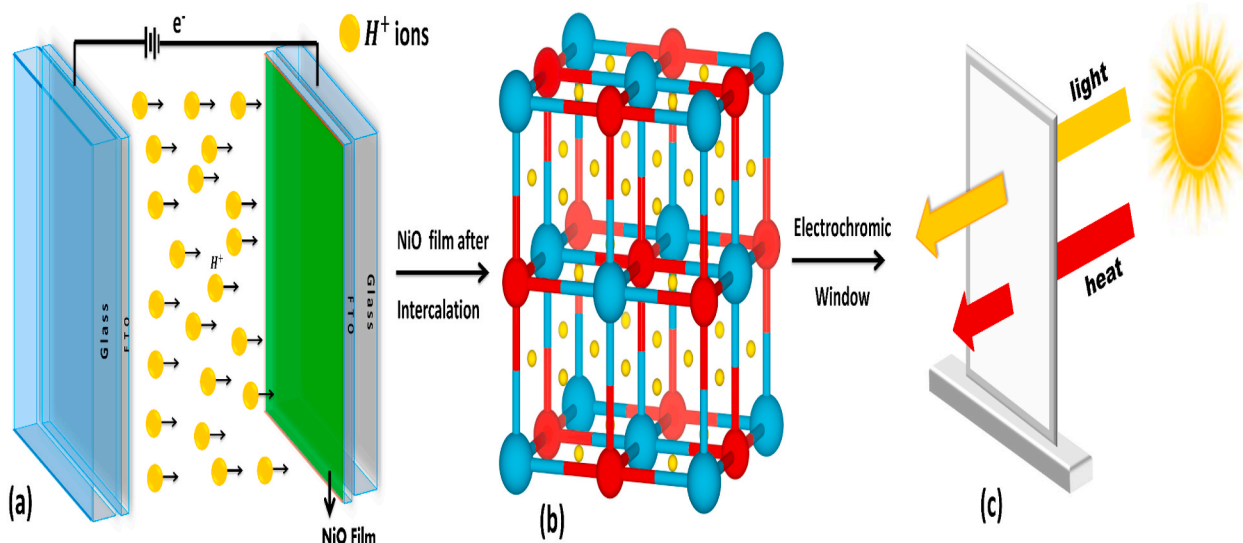


Fig. 9. (a) Schematic illustration of electrochromic device based on nickel oxide, (b) cubic nickel oxide with the intercalation of H^+ ions, (c) electrochromic window in the bleached state which allows complete visible and IR radiation

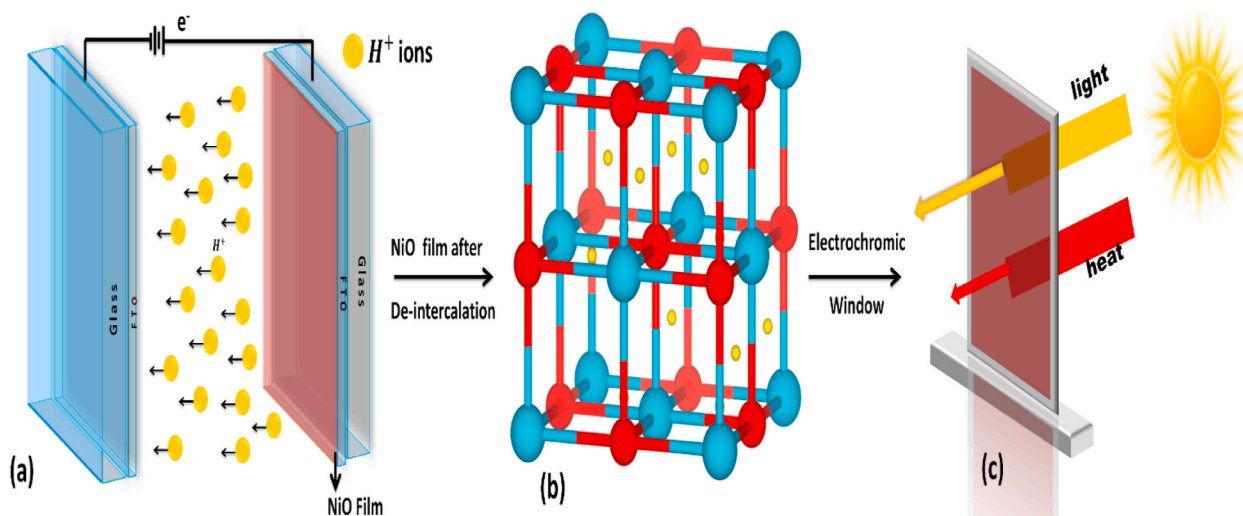


Fig. 10. (a) Schematic illustration of electrochromic device based on nickel oxide, (b) cubic nickel oxide with the de-intercalation of H^+ ions, (c) electrochromic window in the colored state which partially blocks visible and IR radiation

$$\text{Reversibility} = \frac{Q_{di}}{Q_{in}} \quad (5)$$

The efficiency of the electrochromic device is determined by its high optical modulation with less charge intercalation. The observed Q_{in} values are in terms of millicoulombs, representing very little charge intercalation. Also, as observed from table 4, when the concentration of propionic acid is increased from 0.1 to 0.5 M, the quantity of H^+ ions increases, which in turn increases the quantity of charge interaction (Q_{in}). Also, Q_{di} values are less than Q_{in} , which infers that some of the ions are trapped inside the NiO film. The reversibility of the film cycled in 0.5 M propionic acid, as given in table 4 and is found to be more than 73 %, inferring the better quality of the electrochromic device.

In electrochromic devices, shorter switching responses indicate better performance. The response time can be analysed using a chronoamperometry (CA) study. Fig. 11 (b) depicts CA curves for the samples cycled in 0.1 and 0.5 M propionic acid. As shown in table 4, very high switching speeds are achieved for the deposited films, which are faster than the reported values [42,70–73]. It is evident from the observed low values of response time for coloration (t_c) and bleaching

(t_b) that H^+ ions easily get inserted and de-inserted into the NiO matrix. Also, as witnessed in Fig.11 (b), the bleaching speed is more rapid than the colouring speed. This difference is due to the fact that the transition from less conductive NiO to highly conductive Ni_2O_3 is slower during the colouring process than the transition from Ni_2O_3 to NiO. Because of this, H^+ ions get easily intercalated during the bleaching mechanism rather than de-intercalation during the colouring mechanism.

The optical modulation (ΔT) refers to the difference in film transmittance between the bleached state (T_b) and the colored state (T_c), at a wavelength of 550 nm. The optical modulation for the nickel oxide films cycled in 0.1 M and 0.5 M PA is shown in Fig. 11 (c) and 11(d). It is evident from these transmittance spectra that NiO films have excellent electrochromic coloration coupled with good optical modulation, indicating their suitability for electrochromic devices. It is evident from table 4 that the film cycled in 0.5 M PA showed maximum optical modulation of 60 %.

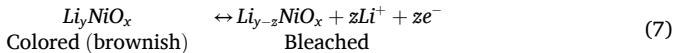
Table 3
Extracted electrochemical parameters of NiO thin films cycled in 0.1 M and 0.5 M propionic acid (PA).

Molarity	Scan rate (mV/s)	Peak current		Diffusion coefficient (D) (cm ² /s)	
		<i>i</i> _{pa} (μA)	<i>i</i> _{pc} (μA)	for <i>i</i> _{pa}	for <i>i</i> _{pc}
0.1 M	25	13.83	18.86	1.03 × 10 ⁻¹³	1.92 × 10 ⁻¹³
	50	21.90	34.35	1.29 × 10 ⁻¹³	3.18 × 10 ⁻¹³
	100	31.61	58.93	1.35 × 10 ⁻¹³	4.69 × 10 ⁻¹³
	150	37.65	59.61	1.27 × 10 ⁻¹³	3.20 × 10 ⁻¹³
0.5 M	25	5.58	19.46	6.75 × 10 ⁻¹⁶	8.18 × 10 ⁻¹⁵
	50	8.50	29.74	7.82 × 10 ⁻¹⁶	9.56 × 10 ⁻¹⁵
	100	13.81	47.96	1.03 × 10 ⁻¹⁵	1.24 × 10 ⁻¹⁴
	150	17.81	58.39	1.14 × 10 ⁻¹⁵	3.07 × 10 ⁻¹³

3.9. Intercalation/de-intercalation of Li⁺ ions

The NiO thin films that had been deposited over an FTO substrate have been cycled through 0.5 and 1.0 M LiClO₄·PC. At varied sweep rates, including 25, 50, 100, and 150 mV/s, CV investigations were

conducted and displayed in Fig. 12 (a, b). In comparison to Ag/AgCl, the scanning potential range has been changed from −1.4 to 2.2 V. The intercalation and de-intercalation of Li⁺ ions are responsible for the film’s bleaching and colouring, respectively. The following are equations illustrating how the optical density changes as Li⁺ ions intercalate and de-intercalate in electrochromic NiO films:



During cathodic scanning between 2 and -1.4 V simultaneously, electrons and Li⁺ ions are intercalated into the NiO film, causing Ni³⁺ to be reduced to Ni²⁺, which results in film bleaching. During the anodic potential scanning between -1.4 and 2 V, Li⁺ ions de-intercalate from the film, causing brown coloration due to the oxidation of Ni²⁺ to Ni³⁺.

The evaluated *i*_{pa}, *i*_{pc}, and diffusion coefficient (D) values for the films were cycled in 0.5 and 1.0 M LiClO₄·PC solutions were provided in table 5, respectively. As the scan rate increases, the values of *i*_{pa} and *i*_{pc} increase. With an increasing sweep rate, Li⁺ ions are intercalated and de-intercalated in NiO film more rapidly.

Fig. 12(c) illustrates the chronocoulometry (CC) curves for the samples cycled in 0.5 M and 1 M LiClO₄·PC. The evaluated *Q*_{in} values are given in table 4. The chronoamperometry studies carried out for the films cycled with 0.5 M and 1 M LiClO₄·PC are given in Fig. 12(d). CA studies were performed with a potential sweep between 0 V and 2.2 V

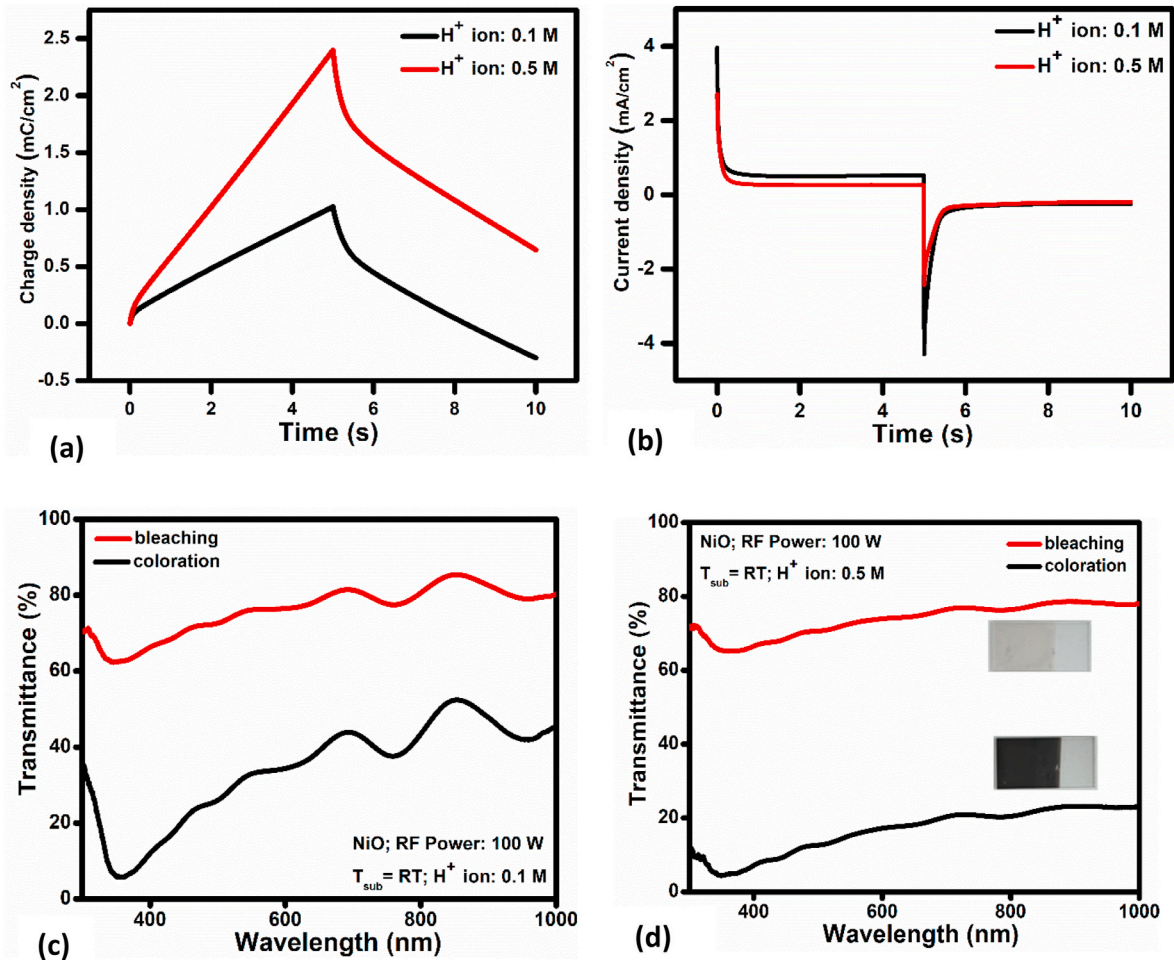


Fig. 11. (a) Chronocoulometry curve of NiO film cycled in 0.1 M and 0.5 M PA, (b) Chronoamperometric curve of NiO film cycled in 0.1 M and 0.5 M PA, (c) Transmittance spectra of NiO film in the bleached and colored states cycled in 0.1 M PA, (d) Transmittance spectra of NiO film in the bleached and colored states cycled in 0.5 M PA.

Table 4
Electrochromic parameters of NiO thin films deposited on FTO substrate.

Electrolyte	T _b (%)	T _c (%)	ΔT	Q _{in} (mC/cm ²)	Q _{out} (mC/cm ²)	Reversibility (%)	t _b (sec)	t _c (sec)
0.1 M PA	76	32	44	1.04	0.312	70	1.25	1.35
0.5 M PA	77	17	60	2.38	0.657	73	0.55	0.95
0.5 M LiClO ₄ -PC	88	68	20	4.91	2.26	55	1.35	1.60
1 M LiClO ₄ -PC	91	64	27	5.00	1.73	65	1.53	1.66

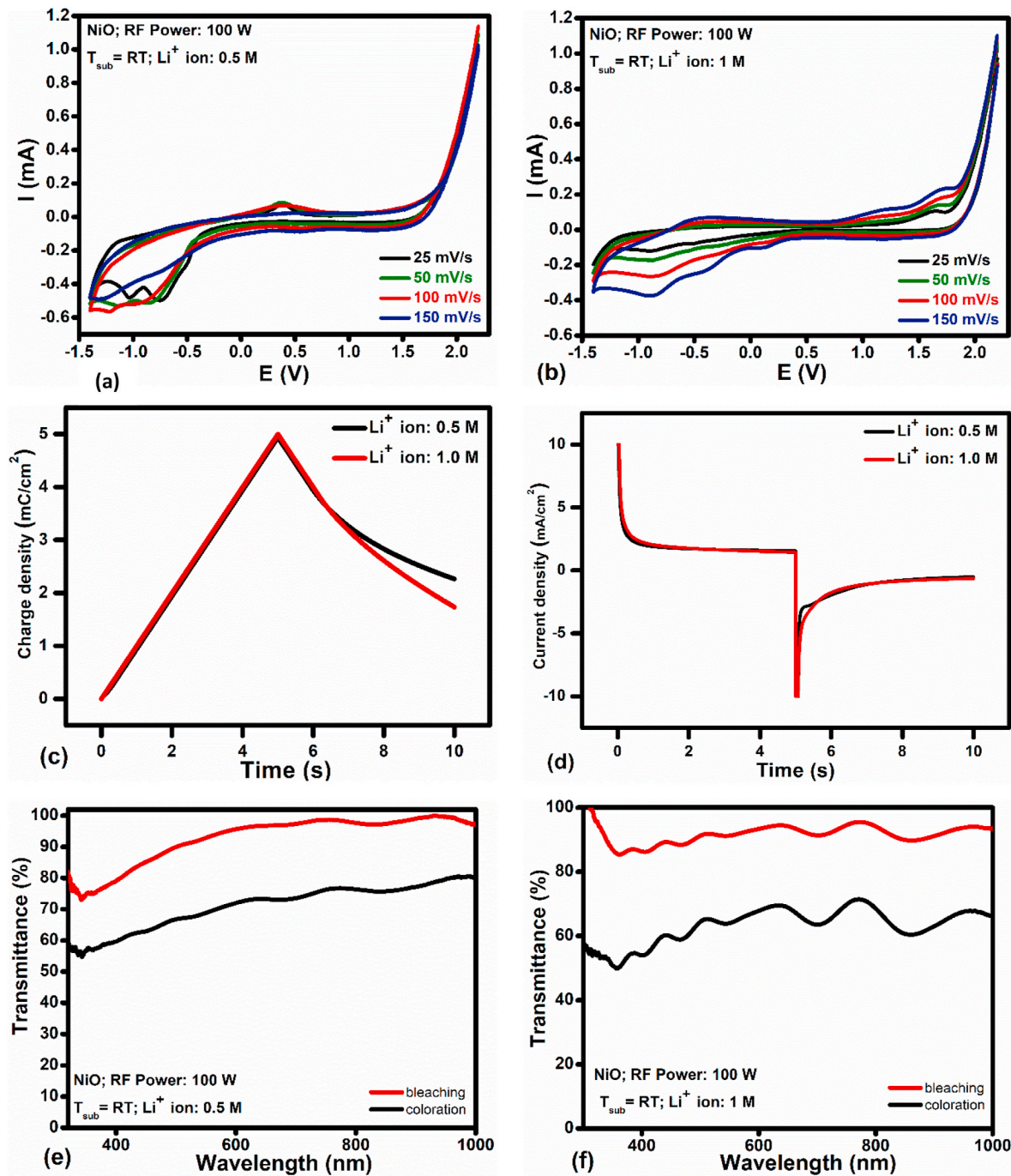


Fig. 12. (a) Cyclic voltammograms of NiO film cycled in 0.5 M LiClO₄-PC, (b) Cyclic voltammograms of NiO film cycled in 1 M LiClO₄-PC, (c) Chronocoulometry curve of NiO film cycled in 0.5 M and 1 M LiClO₄-PC, (d) Chronoamperometric curve of NiO film cycled in 0.5 M and 1 M LiClO₄-PC, (e) Transmittance spectra of NiO film in the bleached and colored states cycled in 0.5 M LiClO₄-PC, (f) Transmittance spectra of NiO film in the bleached and colored states cycled in 1 M LiClO₄-PC

Table 5
Extracted electrochemical parameters of NiO thin films cycled in 0.5 M and 1 M LiClO₄-PC electrolyte solution.

Molarity	Scan rate (mV/s)	Peak current		Diffusion coefficient (cm ² /s)	
		i _{pa} (mA)	i _{pc} (mA)	for i _{pa}	for i _{pc}
0.5 M	25	2.18	0.48	1.02 × 10 ⁻¹⁰	5.08 × 10 ⁻¹²
	50	2.32	0.51	5.82 × 10 ⁻¹¹	2.91 × 10 ⁻¹²
	100	2.44	0.55	3.21 × 10 ⁻¹¹	1.68 × 10 ⁻¹²
	150	2.42	0.48	2.11 × 10 ⁻¹¹	2.08 × 10 ⁻¹¹
1 M	25	1.03	19.7	5.77 × 10 ⁻¹²	2.09 × 10 ⁻¹³
	50	1.06	24.5	3.01 × 10 ⁻¹²	1.62 × 10 ⁻¹³
	100	1.09	28.9	1.59 × 10 ⁻¹²	1.13 × 10 ⁻¹³
	150	1.10	34.8	1.09 × 10 ⁻¹²	1.09 × 10 ⁻¹¹

(coloration) and then reversed to −1.4 V (bleaching). From the Fig. 12 (d), it is evident that the slope of the cathodic current density for all deposited films is slightly higher than the slope of the anodic current density. This shows that the bleaching process occurs faster than the coloration process. Thus, Li⁺ ions are intercalated more easily than de-intercalation.

Fig. 12(e)–(f), respectively, display the optical transmittance spectra of NiO films that have been colored and bleached after being cycled in 0.5 M and 1.0 M LiClO₄-PC electrolyte solutions. The optical modulation of NiO films was computed at 550 nm, which exhibits good optical modulation, and the results are given in table 4. The highest optical modulation achieved was found to be superior to previous reports [71–73].

The performance of the electrochromic device is determined by its high optical modulation with minimal charge insertion, high optical switching speed, and reversibility. Table 4 shows the electrochemical parameters for both the ions. As shown in table 6, the electrochromic performance of our fabricated sample (cycled with 0.5 M of H⁺ ions) is better than the reported values [17,36,71–74]. The results show that a high optical modulation of 60 %, a rapid response time of less than 1 s,

and minimum charge intercalation were observed for the film cycled with 0.5 M of H⁺ ions. Also, compared to H⁺ ions, a decrease in the optical modulation was observed for the film cycled with Li⁺ ions, irrespective of the concentration of electrolytes. The intercalation/de-intercalation mechanism of Li⁺ ions is a little slower compared to H⁺ ions because the ionic radius of H⁺ is small compared to Li⁺ ions. The larger ions diffuse more slowly into the film. This causes strong and reversible coloration when using the lighter H⁺ ion than the heavier Li⁺ ion. Similar results have been observed by K.J. Patel et al. for H⁺, Na⁺, and K⁺ ions [45]. Similar results have been reported for H⁺, Li⁺, and K⁺ ions by Lee [68].

Eventually, a durability evaluation was performed on a deposited nickel oxide thin film by subjecting it to 1000 voltametric cycles in a 0.5 M propionic acid solution, using a scan rate of 50 mV/s. Fig. 13 depicts data indicating that there have been little changes over time, but the system has remained mostly stable for up to 1000 cycles. Hence, it is evident from the results that the prepared films exhibit excellent electrochromic behaviour.

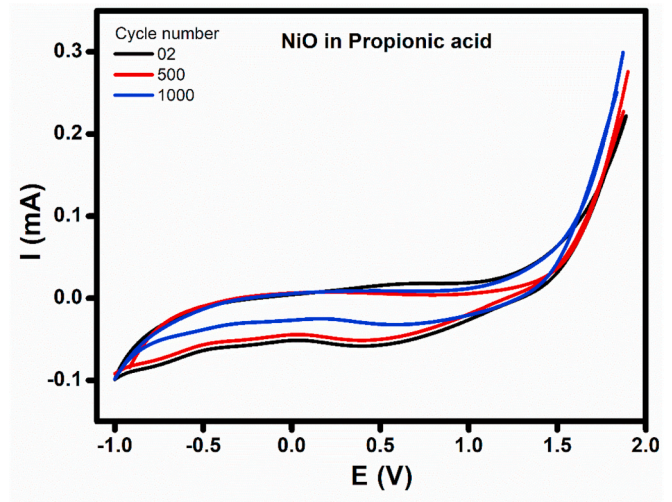


Fig. 13. Cyclic voltammograms for NiO film in 0.5 M PA; the voltage sweep rate was 50 mV/s

Table 6
Comparison table of comparing our nickel oxide thin film’s electrochromic performance with other reported values.

Material	Technique	Electrolyte	Bleached (T _b) %	Colored (T _c) %	Optical modulation (ΔT) %	Colouring time (sec) t _c	Bleaching time (sec) t _b	Ref
NiO	sputtering	Li ⁺	75	15	60.0	0.95	0.55	Current work
NiO	CBD	OH ⁻	–	–	69.4	2.6	1.6	[31]
NiO	sputtering	Ta ₂ O ₅	73.4	6.6	66.8	5.0	17.7	[17]
NiO	solvothermal	OH ⁻	45.4	0.3	45.1	6.8	2.3	[71]
NiO	Electro chemical lithiation	Li ⁺	–	–	24.3	6.9	1.6	[72]
NiO	hydrothermal	OH ⁻	44.3	0.09	44.2	14.7	5.4	[73]
NiO	CBD	OH ⁻	–	–	54.5	10.4	7.9	[68]
NiO	Sputtering	OH ⁻	62.38	23.07	39.3	1.34	1.17	[74]
NiO	Sputtering	Li ⁺	–	–	50	2.6	4.2	[75]
NiO	e-beam evaporation	Li ⁺	–	–	27.8	–	–	[50]
Ta–NiO	Sputtering	Li ⁺	–	–	43.5	17	8	[76]
V–NiO	hydrothermal	OH ⁻	–	–	35.5	12.8	9.6	[77]
W–NiO	Sputtering	Li ⁺	–	–	61.56	1.40	4.42	[78]
W–NiO	Sputtering	Li ⁺	–	–	83	5.5	7	[79]
NiO	Sputtering	OH ⁻ + Li ⁺	–	–	61	–	–	[80]
Zn–NiO	hydrothermal	OH ⁻	–	–	68.57	6.4	3.8	[81]
Hf–NiO	spray pyrolysis	OH ⁻	–	–	49	4.67	3.58	[82]
NiO/Ni(OH) ₂	hydrothermal	OH ⁻	–	–	87.4	7.2	5.8	[83]

4. Conclusions

In conclusion, we have fabricated a highly efficient NiO electrochromic device using the RF magnetron sputtering technique. The NiO thin films deposited on the FTO substrate at room temperature with 100 W of RF power showed less crystalline or near amorphous nature. AFM revealed the homogenous, pinhole free nature of the film with an R_{rms} value of 0.736 nm. Raman bands were detected at 560 cm^{-1} and 1100 cm^{-1} , representing first and second-order LO modes, which confirms the presence of defects. XPS analysis revealed the existence of Ni^{2+} ions along with some Ni^{3+} ions. An optical transparency of 85 % is achieved with a bandgap of 3.12 eV. RTPL spectra revealed NBE emission at 365 nm and excitonic emission at 420 nm, which infers the existence of defects in the film. The presence of defects facilitates easy intercalation and de-intercalation processes, which in turn enhance the electrochromic performance. Highly enhanced electrochromic properties, such as better optical modulation of 60 % at 550 nm, and rapid switching speeds (0.55s for bleaching and 0.95s for coloration) have been achieved for film cycled with 0.5 M H^{+} ions when compared to film cycled with Li^{+} ions. Since the ionic radius of H^{+} is small compared to Li^{+} ions, stronger and reversible coloration was observed for the lighter H^{+} ions than the heavier Li^{+} ions. Therefore, based on our results, we believe that the deposited NiO films, which have a near amorphous structure along with defects in the form of nickel vacancies, are very ideal to use in electrochromic devices.

CRediT authorship contribution statement

K.S. Usha: Writing – review & editing, Writing – original draft, Data curation, Conceptualization. **Sang Yeol Lee:** Writing – review & editing, Supervision, Investigation, Conceptualization. **R. Sivakumar:** Writing – review & editing, Validation, Supervision, Investigation, Conceptualization. **C. Sanjeeviraja:** Writing – review & editing, Validation, Supervision, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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