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Enhanced Coloration for Hybrid Niobium based Electrochromic Devices

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ABSTRACT: Niobium pentoxide, Nb₂O₅, exists in many polymorphs with diverse properties and morphologies that are dependent on the synthesis route. In this work, we design a new approach to fabricate and stabilize the metastable polymorph hexagonal niobium pentoxide using soft chemistry and in particular the polyol synthesis. The electrochromic properties of homogeneous niobium pentoxide thin films deposited by Dip Coating, from as-synthesized hexagonal powder, are studied in lithium trifluoromethanesulfonimide (LiTFSI) in 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMITFSI) ionic liquid electrolyte versus Pt as counter electrode. The structure and morphology of the Nb₂O₅ thin films before and after cycling are characterized by *ex-situ* XRD and SEM while their optical and electrochemical properties are investigated by *in-situ* transmittance and cyclic voltammetry (CV), respectively. Thin films made from hexagonal Nb₂O₅ with spheres architecture exhibit good cycling stability, high transmittance modulations ($\Delta T \approx 33\%$ at 550 nm), fast switching speeds (2 to 3 s for coloration and bleaching at 550 nm), and high coloration efficiency ($CE \approx 26 \text{ cm}^2 \cdot \text{C}^{-1}$) with a good quality factor $G_{(\lambda)} = 10.4 \text{ cm}^2 \cdot \text{C}^{-1} \cdot \text{s}^{-1}$. Finally, novel electrochromic devices based on hybrid thin films combining PEDOT:PSS and oxides are assembled showing enhanced coloration and simultaneous color change due to their double sided configuration.

I. Introduction

Currently, more than 40% of the energy consumption in buildings either for heating or cooling, but this phenomenon is always accompanied by a rejection of carbon dioxide, CO₂. To improve the energy efficiency and reduce the emission of CO₂ into the atmosphere, smart windows, often based on electrochromic materials, offer a promising solution. Electrochromic (EC) materials are characterized by the ability to change their optical properties, when a voltage is applied.¹⁻³ Electrochromism occurs in a number of organic⁴, inorganic⁵ and hybrid materials⁶, allowing to address multiple applications either in a transmittive mode (smart windows...) or reflective one (displays...). In comparison to others, the family of inorganic oxides is commonly known for its good stability. Another advantage specificity lies in the facility to improve the electrochromic properties by single or double doping or by addition of other materials and formation of composites.^{7,8}

Since the discovery of electrochromism in Nb₂O₅ in 1980, by Reichman and Bard⁹, niobium oxide has been studied extensively and has come up as a promising electrochromic material in respect of chemical stability in many electrolytes, nice reversible colors switching and long-term cycling stability.^{10,11} Niobium element characterized by several valence states from +2 to +4 to +5 for NbO, NbO₂ and Nb₂O₅, respectively¹², exists in various oxides polymorphic forms including monoclinic (H-Nb₂O₅), tetragonal (M-Nb₂O₅), orthorhombic (T-Nb₂O₅), and pseudo hexagonal (TT-Nb₂O₅). The different crystal phases of

Nb₂O₅ depend on the synthesis temperature. For example a low temperature (≈ 200 °C) leads to an amorphous phase further crystallizes at 500 °C into hexagonal or orthorhombic phases, while at medium-temperature (≈ 800 °C) niobium oxide transforms into the tetragonal phase and forms the monoclinic phase above 1000 °C^{13,14}. Herein, we present a novel synthesis route to stabilize the metastable phase (TT-Nb₂O₅) with ultrafine powders and we demonstrate the electrochromic performance of this metastable allotropic form of niobium pentoxide.

In the literature, a variety of approaches have been employed to fabricate Nb₂O₅ nanostructures such as hydro/solvothermal¹⁵ and sol-gel, but these methods have the inconvenience of limited reproducibility and scaling up. To solve this issue, new synthesis methods able to produce a large quantity of nanometric powders with high reactivity are highly needed. As one of the solution methods, the polyol synthesis has been initially developed for metals^{16,17} and more recently applied to the synthesis of single-crystalline oxide nanostructures¹⁸. This low reaction temperature method, in which the polyol serves as both the solvent and the reducing agent, offers several advantages as compared to other chemical methods. Among them a non-exhaustive list contains (i) water-comparable solubility of simple metal-salt precursors; (ii) high boiling points (up to 320 °C); (iii) reducing properties for the instantaneous synthesis of metals; (iv) coordinating properties for surface functionalization and colloidal stabilization of nanoparticles; (v) wide adaptability of the polyols ranging from low-weight ethylene glycol (EG)

to high-weight polyethylene glycols (PEGs) (vi) high-quality doped powders with specific morphologies (vii) applicable to large scale manufacturing processes. In summary, this process is ideal for the processing of very fine powders having high purity, high crystallinity, excellent reproducibility, narrow particle size distribution, uniformity, and high reactivity.¹⁹

The electrochromic performance of niobium pentoxide depends on several parameters including the morphology and the porosity, the film thickness, the surface roughness and the deposition method. Various deposition techniques including spray pyrolysis²⁰ radio-frequency magnetron sputtering²¹, pulsed laser deposition²², chemical vapour deposition²³ and Dip-coating techniques^{12, 24} have been used to prepare Nb₂O₅ thin films. Among them, Dip Coating processes present the advantage of high versatility, low cost, reasonable deposition rates, and simplicity in experimental parameter modulation. In this study, niobium pentoxide (Nb₂O₅) thin films were dip coated from nanopowders synthesized from a single polyol route. Herein, their electrochromic activity in lithium-based electrolyte is discussed in terms of optical contrast, cyclability, and stability. Their nice EC properties allow further integration of this oxide in complete devices optimized in respect of novel architecture and enhanced coloration.

During the recent decade, escaping from the common 5-layers battery type devices, remarkable progress have been achieved in exploring new concepts to enlarge the field of applications for electrochromic devices. Such evolution includes the development of new EC materials as well as novel architectures. For instance, in 2017 our group²⁵ reported for the first time a double sided electrochromic device based on Metal-Organic Frameworks (MOFs). Mixing the advantages of inorganic and organic materials, hybrids systems offer great potential of exploration. Indeed, while transition metal oxide (TMOs) have generally a good redox activity with high optical properties and good memory effect, they suffer, among other things from a too low electrical conductivity. On the contrary, polymer-based electrochromic films are characterized by rapid kinetics and multi-color electrochromism, while they typically show poor adhesion to the substrate. To counter balance the pros and cons of both types of materials, we suggest mixtures of metal oxide and polymer as good candidates for electrochromic application^{26, 27}. The benefit of such approach has been recently demonstrated through various examples. Among those hybrid composite materials, mixtures of PEDOT:PSS and WO₃²⁸ or with TiO₂²⁹ are characterized by good properties. Furthermore, the combination of PEDOT:PSS and V₂O₅ in electrochromic device shows better stability as compared to a pristine PEDOT:PSS-based device^{30, 31}. Recently, Mishra and al., have shown that TiO₂-Co₃O₄ core-shell has a good electrochromic behavior and superior supercapacitive properties.³² In the same context, Zhang and al., reported that the organic-inorganic nanocomposites (ATO/TiO₂@PANI)³³ present better electrochromic performance compared with pure PANI film. According to the authors the improved electrochromic properties are mainly attributed to the core/shell structure, formation of the donor-acceptor system. Based on this finding, we successfully combine two hybrids films (namely Nb₂O₅ - PEDOT:PSS and V₂O₅-PEDOT:PSS) to build for the first time a hybrid electrochromic device with dual face.

II. Experimental details

II.1. Polyol synthesis of Nb₂O₅ powder and characterization

All of the chemical reagents were purchased from Acros Organics and utilized without further purification. Ammonium niobate (V) oxalate hydrate was used as niobium source and diethylene glycol (DEG) as template. In a typical synthesis, C₄H₄NNbO₉ · H₂O (7.574 g) was added to 250 mL of C₄H₁₀O₃. The resulting mixture was heated to 110 °C with continuous stirring to give a white solution that was refluxed at 160 °C for 1 h. At the end of the reaction, a white precipitate was obtained. The precipitate was centrifuged and washed several times with ethanol to remove the organic product and dried in an oven at 80 °C. To prepare the final Nb₂O₅ powders, the precipitates were calcined for 1 h at 500 °C.

The powder structure was characterized by X-ray diffraction analysis (Philips PW 1820, PANalyticalX'Pert instrument, 2θ range from 15 to 60° and λ_{CuKα1} = 0.154056 nm). The unit cell parameters were refined by structural pattern matching using the Fullprof program package. Transmission electron microscopy (TEM) images were recorded with a SEI instrument (operating at 5 kV) microscope.

II.2. Film preparation and characterization

Nb₂O₅ films were deposited by the dip coating method from homemade powder, synthesized by the polyol process. Firstly, 2.5 g of powder was dispersed into 5 ml ethanol. The resulting dilute was stirred for 1 h at room temperature and after aliquots of the as-prepared colloidal Nb₂O₅ solution were deposited on the ITO (In₂O₃:Sn) coated glass (commercialized by SOLEM with a resistance of 30 Ω/□). The thickness of the Nb₂O₅ films, measured using a Dektak mechanical profilometer, was of about 800 nm ± 50 nm. For the identification of the crystal phases of the thin films before and after cycling, X-ray diffraction (XRD, Philips PW 1820, PANalyticalX'Pert instrument, 2θ range from 15 to 60° and λ_{CuKα1} = 0.154056 nm) was used.

The morphology of the layers before and after cycling was investigated using a JEOL JSM-840 (operating at 15 kV) microscope.

II.3. Electrochromic measurements

Electrochemical measurements of Nb₂O₅ thin films on ITO/glass were carried out in a three electrodes cell configuration using a BioLogic SP50 potentiostat/galvanostat apparatus. The counter-electrode and reference electrode consisted of a platinum foil and Saturated Calomel Electrode, SCE (E_{SCE} = 0.234 V/ENH), respectively. The operating voltage was controlled between -1.1 and -0.1 V at a scan rate of 20 mV/s, in lithium based electrolyte, namely, lithium bis-trifluoromethanesulfonimide (LiTFSI, Solvionic, purity N99.99%) in 1-ethyl-3-methylimidazoliumbis-(trifluoromethanesulfonyl)-imide (EMITFSI, purity N 99.99%). All the electrochemical measurements were performed at room temperature. The optical transmittance of Nb₂O₅ thin films was measured *in-situ* using a Varian Cary 5000 UV-Vis-NIR spectrophotometer.

III. Results and discussion

III.1. Polyol synthesis of Nb₂O₅ powder

The crystallinity of the powder synthesized by the polyol process pre- and post-calcined under air was analyzed by XRD (Figure 1). Prior to calcination, the XRD pattern (Figure 1a), with no visible peaks, corresponds to an amorphous phase, in agreement with R.A. Rani et al.¹⁴, reporting amorphous Nb₂O₅ at low temperature (≈200 °C). As the temperature of the calcination increases, niobium oxide becomes crystallized. At 400

°C, (**Figure 1b**), the XRD pattern reveals the presence of a predominantly amorphous phase with the appearance of a single peak characteristic of the hexagonal phase of Nb₂O₅. An increase in temperature to 500 °C (**Figure 1c**) leads to a well crystallized phase with narrow X-ray peaks. The d-spacing values of all diffraction peaks are identical to those of the hexagonal crystalline phase Nb₂O₅ with lattice constants a = b = 3.6070 Å, and c = 3.9250 Å (JCPDS # 28-0317). The absence of any additional peaks from other phase or impurity indicates that Nb₂O₅ with high purity can be synthesized via the polyol synthesis at 160 °C for 1 h. The hexagonal phase remains predominant after a post-thermal treatment at 600 °C (**Figure 1d**) with the appearance of some small peaks characteristic of orthorhombic Nb₂O₅.

From the temperature study, a treatment of the powders obtained by polyol process at 500 °C for 2 h under air was established as optimal conditions to synthesize the metastable Nb₂O₅ hexagonal phase with high crystallinity chosen for further investigation.

The average crystallite size was calculated using the Scherrer's formula:

$$L = 0.89\lambda/\beta \cos\theta$$

Where L is the average crystallite size in nm, $\lambda=0.154056$ nm, β is the full width at the half maximum, and θ is the diffraction angle. The average crystallite size value, calculated from three of the main peaks of the XRD pattern, is about 9 nm.

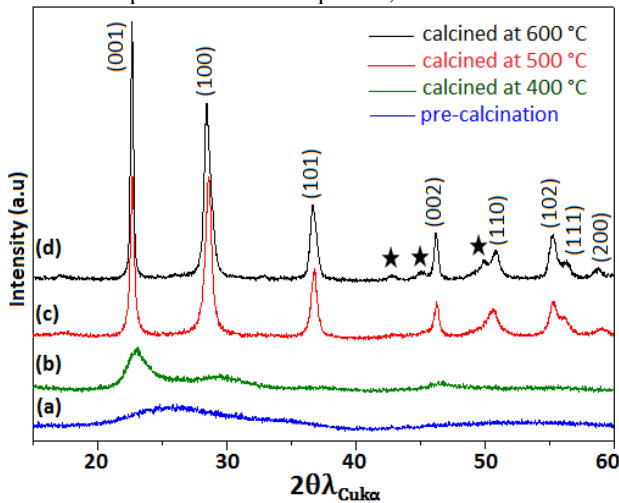


FIGURE 1. XRD patterns of the niobium oxide powders synthesized by polyol process (a) pre-calcination and post-calcination at (b) 400 °C, (c) 500 °C and (d) 600 °C under air for 2 h. (★) correspond to orthorhombic Nb₂O₅.

Figure 2 shows the corresponding TEM images of the powders elaborated by the polyol process. The hexagonal Nb₂O₅ phase is homogenous with particles regularly sized and which display 2D nanospheres morphology, with a radius ranging from 10 nm to 35 nm.

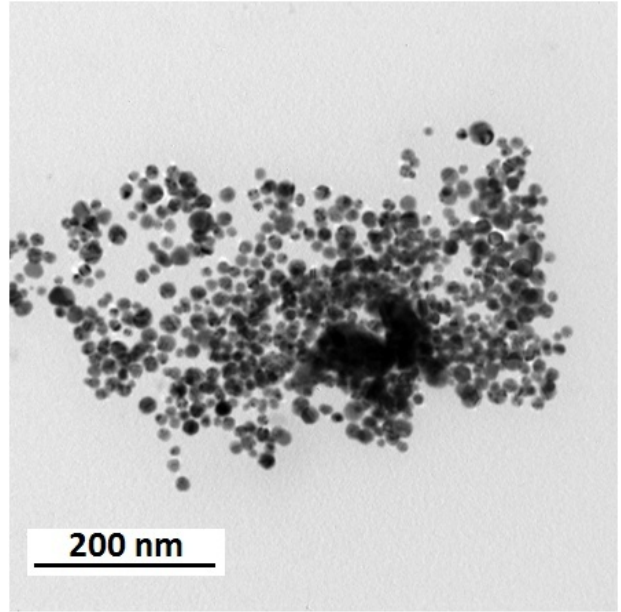


FIGURE 2. TEM images of hexagonal Nb₂O₅ powder after thermal treatment at 500 °C for 2 h under air.

To complete the structural studies, refinement using an isotropic peak profile function (Caglioti function) was carried out on the hexagonal Nb₂O₅ compound (**Figure S1**). Unit-cells parameters and the reliability factors (R_p , R_{wp} , and R_{exp}) are summarized in **Table S1**. The isotropy of the structure well agrees with the isotropy of the morphology.

III.2. Electrochromic properties of Nb₂O₅ thin films

III.2.1. Cyclic voltammetry (CV) measurements

An important requirement of electrochromic materials is their stability upon cycling while keeping their structural integrity. The repetitive cycling of Nb₂O₅ thin film in LiTFSI-EMITFSI ionic liquid at a scan rate of 20 mV/s between -1.1V as -0.1V shows good reversibility and cyclability (**Figure 3a** and inset **Figure 3a**). No significant degradation corresponding to only 1 % decrease of the capacity after 100 cycles (inset **Figure 3a**) confirms this good stability. Upon cathodic and anodic sweeping, the transparent films show one-step electrochromism from transparent to blue (**Figure 3b**). The color change is accompanied by the appearance of a well-defined oxidation peak located at -0.63V. During the cathodic scan a simultaneous insertion of electrons and Li⁺ ions into the Nb₂O₅ film causes the reduction of Nb⁵⁺ to lower valence state, Nb⁴⁺ and hence the film coloration. In its reduced state, the film appears blue. During the anodic scan, the deinsertion of Li⁺ ions causes the bleaching of the film that becomes transparent. As reported in the literature^{24, 34}, the redox chemical reaction associated with coloration and bleaching in Nb₂O₅ films can be schematized as follows:



The number of exchanged Li⁺(x) involved during each coloration/bleaching process was estimated using the following equation: $Q = F \cdot n(\text{Nb}_2\text{O}_5) \cdot x$, where Q is the electrochemical capacity, F = 96500 C, and n is number of moles. Assuming a density close to 100 %, x value of about 2 was calculated suggesting the participation of all Nb ions in the Nb⁵⁺ to Nb⁴⁺ redox process.

After 100 cycles, negligible shift in the position of the oxidation peaks was observed. The origin of such deviation remains unclear but might be ascribed to a modification of the film morphology upon cycling.

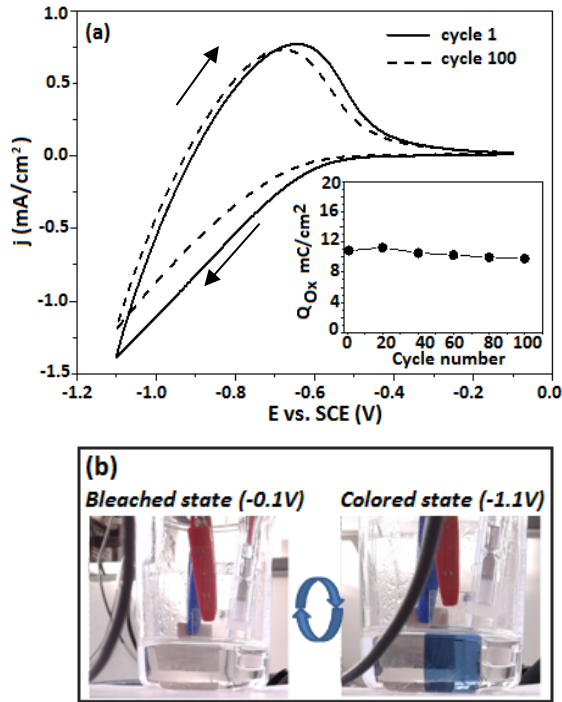


FIGURE 3. The 1st and the 100th cyclic voltammograms for the Nb₂O₅/LiTFSI in EMITFSI/Pt/SCE recorded at 20 mV/s scan rate (a), Corresponding variation of the anodic capacity upon cycling (inset Fig. 3a) and Visual appearance of Nb₂O₅ films in the bleached and colored states (b).

III.2.2. Optical properties

The *in-situ* transmittance upon cycling of Nb₂O₅/LiTFSI in EMITFSI/Pt/SCE is displayed in **Figure 4**. The colored-blue state (-1.1 V) and the bleached-transparent state at (-0.1V) are associated with transmittance values of about $T_c \approx 55\%$ and $T_b \approx 88\%$ at 550 nm, respectively, corresponding to a total optical transmittance modulation of $\Delta T \approx 33\%$. The electrochromic performance is commonly characterized by the optical density (OD) represented by the logarithmic ratio of the transmittance in the bleached state (T_b) to the transmittance in colored state (T_c) and the coloration efficiency (CE) defined as the change in optical density per unit-inserted charge. The ΔOD and coloration efficiency (CE) are calculated using the two relations:

$$\Delta OD = \log(T_b/T_c)$$

Where, T_b and T_c are the transmittance of the Nb₂O₅ film in the bleached and colored states, respectively.

$$CE = \Delta OD/Q$$

Where, Q is the amount of charge transferred per unit area. From calculated optical density ($\Delta OD = 0.205$) and the amount of charge ($Q = 0.008 \text{ C/cm}^2$), a coloration efficiency $26 \text{ cm}^2/\text{C}$ is obtained. Such values nicely compared with values reported in the literature^{34, 35} (Table 1).

The switching optical response in between alternating potentials is a key characteristic of electrochromic materials. The switching kinetics of Nb₂O₅ thin film was deduced from monitoring the transmittance at a wavelength of 550 nm under the application of potentials window of -1.1 V and -0.1 V at 10 mV/s. The response times, slightly higher in the bleaching process (3 s) than in the colored one (2 s), due probably to the transition from the semiconductor (Nb₂O₅) to conductor (Li_xNb₂O₅) while the process is faster from a conductive to a semi-conductive behavior, remain of few seconds.

To appraise the overall EC performances of the Nb₂O₅ films, we calculated a quality factor $G_{(\lambda)}$ using the relation:³⁶

$$G_{(\lambda)} = CE_{(\lambda)} / \tau, \tau = (\tau_c + \tau_b) / 2$$

The value of $G(550 \text{ nm})$ for a Nb₂O₅ thin films is $10.4 \text{ cm}^2 \cdot \text{C}^{-1} \cdot \text{s}^{-1}$. This value, not reported in the literature to our knowledge for Nb₂O₅, is 2.54 times as high as the one of typical electrochromic oxide WO₃³⁶.

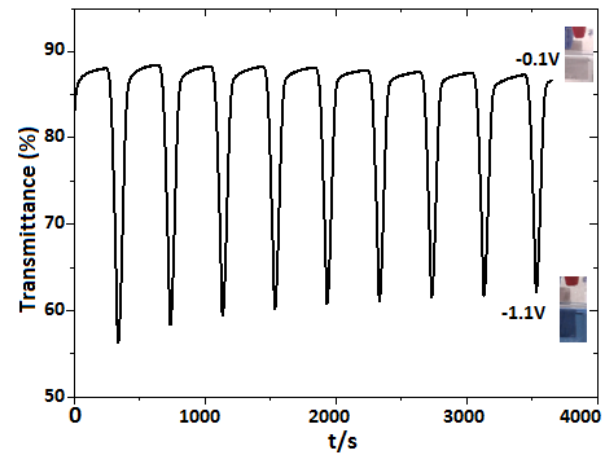


FIGURE 4. Transmittance curves of the Nb₂O₅/LiTFSI in EMITFSI/Pt/SCE recorded *in situ* at 550 nm with voltammetry cyclic range -1.1 V to -0.1V.

In summary, the comparison of the electrochromic characteristic of Nb₂O₅ thin films with the ones reported in the literature confirm the benefit of the polyol synthesis which leads to very fine and very reactive powder showing higher performances (**Table 1**).

TABLE 1. Comparison of the electrochromic performance of Nb₂O₅ thin films with literature.

Ref.	ΔT (%)	CE ($\text{cm}^2 \cdot \text{C}^{-1}$)	t_c (s)	t_b (s)
Nb ₂ O ₅ [37]	25.4	4.63	---	---
Nb ₂ O ₅ [35]	----	13	3.7	4.7
Nb ₂ O ₅ [24]	----	22	---	---
Nb ₂ O ₅ [21]	----	10	---	---
Nb ₂ O ₅ in this work	33	26	2	3

III.3. Structure and morphology of the Nb₂O₅ films before and after cycling

The XRD pattern of the Nb₂O₅ film deposited by Dip-Coating is shown in **Figure 5a**. The d-spacing values of all diffraction peaks match the ones of the hexagonal crystalline phase (JCPDS# 007-0061) and of the ITO substrate (JCPDS # 44-1087). No major change in XRD peak position compared to Nb₂O₅ powders and no peaks of any other phase or impurity are detected after deposition on ITO substrate, demonstrating a good stability of Nb₂O₅ nanoparticles synthesized by the polyol method using these deposition conditions. **Figure 5b and 5c** shows the XRD of the Nb₂O₅ film in reduced and oxidized state, after 50 cycles. All peaks are indexed to the crystal phase of hexagonal Nb₂O₅ indicating a remarkable stability upon repeated lithium insertion and deinsertion. A close examination of the XRD patterns upon cycling reveals an increase in the width at half height with cycling while in the reduced state the slight shift of the peaks towards low theta values well agrees with an insertion of lithium and the formation of Li_xNb₂O₅ (**Figure S2**). The crystallite size, calculated using the Scherrer formula, for the Nb₂O₅ film as deposited and reduced/oxidized Nb₂O₅ film after 50 cycles is about 30, 20 and 15 nm, respectively.

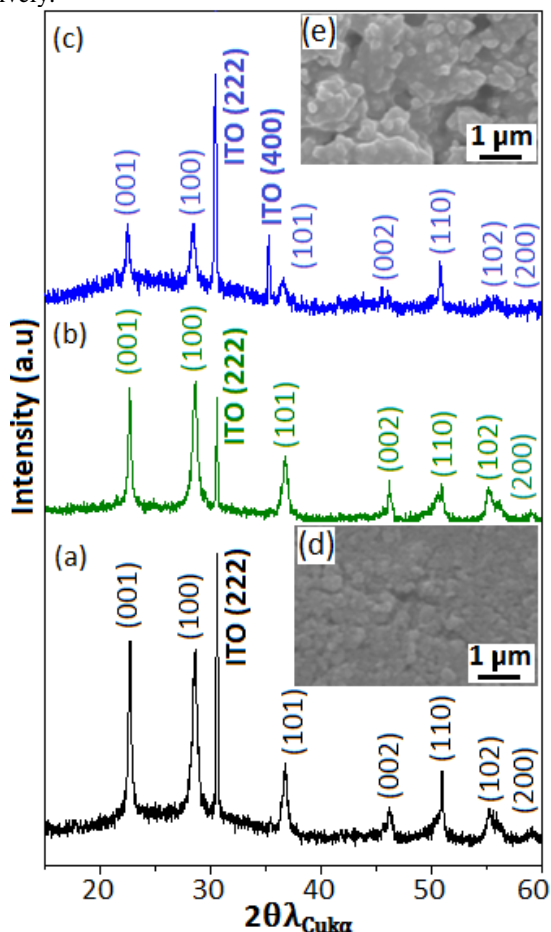


FIGURE 5. XRD patterns of (a) Nb₂O₅ film as-deposited on ITO/glass substrate (b) *ex-situ* XRD patterns of the reduced Li_xNb₂O₅ film and (c) *ex-situ* XRD patterns of the oxidized Nb₂O₅ film after the 50th cycle. SEM images of (d) Nb₂O₅ film as-deposited on ITO/glass substrate and (e) *ex-situ* SEM images of the oxidized Nb₂O₅ film after the 50th cycle.

The SEM analysis of the Nb₂O₅ film before cycling (**Figure 5d**) shows that the Dip Coating deposition leads to homogeneous films of uniform particles with smooth surfaces being relatively densely covered and containing many small cracks. Such morphology, exhibiting a large surface exchange with the electrolytes, appears well suitable for the alkaline elements insertion. SEM imaging of the Nb₂O₅ film after 50 cycles (**Figure 5e**) shows a significant change in the morphology. After cycling, the morphology of Nb₂O₅ film consists of an assortment of small particles that agglomerated giving places to large particles of indefinite forms. Besides the presence of visible voids indicates that upon cycling the electrolyte penetration may be progressively facilitate, promoting the insertion/deinsertion of lithium ions in the Nb₂O₅ matrix.

III.4. Hybrid Electrochromic Devices

III.4.1. Fabrication of hybrid electrochromic Device

Using the common 5-layer type battery device, an electrochromic device consisting of two hybrid electrochromic films separated by an electrolyte was assembled. V₂O₅/PEDOT:PSS and Nb₂O₅/PEDOT:PSS have been employed as the two electrodes and the 60% of (LiTFSI-BMTFSI blended with PMMA) and 40% of TiO₂ (Sigma Aldrich) is used as the electrolyte membrane. The same protocol was utilized to prepared both (Oxide/PEDOT:PSS) electrodes. 70% of oxide nanopowders (Nb₂O₅ or V₂O₅) synthesized by polyol process were mixed with 30% PEDOT:PSS (Sigma Aldrich) in ethanol as solvent (this mass ratio between oxides and PEDOT:PSS was optimized to get the highest contrast in the visible) and then the mixture was stirred for 3 h. After the preparation of the suspension, the dip coating method was used to deposit the Nb₂O₅ (or V₂O₅)/PEDOT:PSS layer on ITO. The two hybrids films were dried in air at room temperature. The ionic electrolyte membrane was prepared by mixing 60% of (LiTFSI-BMTFSI blended with PMMA) and 40% of TiO₂ and then the mixture was stirred for 12 h (**Figure S3**).

The hybrid composite [Nb₂O₅+PEDOT:PSS] film was cycled in the LiTFSI-EMITFSI electrolyte for five cycles and assembled in the blue reduced state to the precycled orange hybrid composite film [V₂O₅+PEDOT:PSS].

III.4.2. Electrochromic performance of the hybrid Device

Figure 6a shows the superposition of the CVs for the two types of devices: (i) inorganic device Li_xNb₂O₅/electrolyte/V₂O₅ and (ii) hybrid device Li_x[Nb₂O₅+PEDOT:PSS]/electrolyte/V₂O₅+PEDOT:PSS] cycled at room temperature in ionic liquid at 10 mV/s. The combination of both cyclic voltammetry as well as *in-situ* reflectance shows higher electroactivity for the hybrid device associated with higher optical contrast. Indeed, the modulation in reflectance of the hybrid device is quite double the one of the inorganic ECD ($\Delta R = 21\%$ for inorganic ECD $\ll 42\%$ for hybrid ECD) (**Figure 6b**). In the following, we focus our attention on the hybrid device.

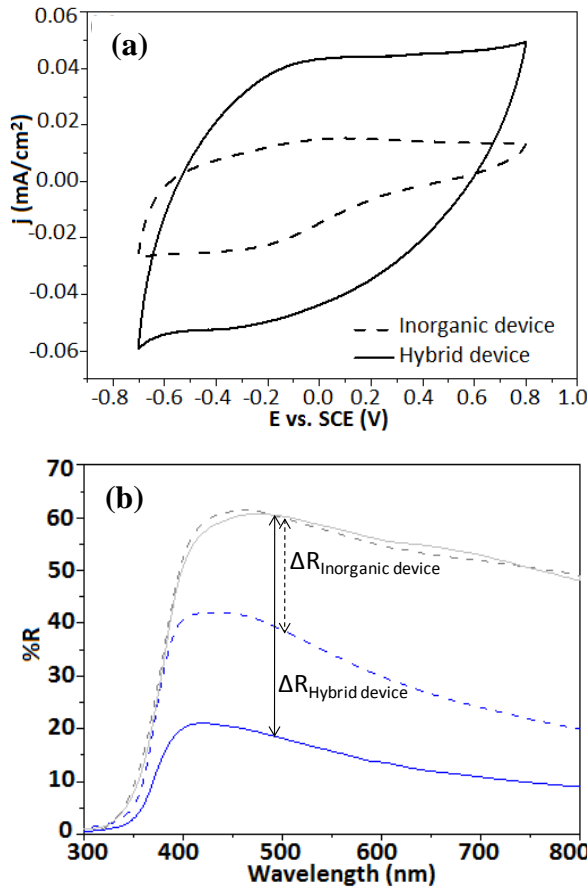


FIGURE 6. Comparison of (a) cyclic voltammograms of the inorganic device ($\text{Li}_x\text{Nb}_2\text{O}_5/\text{electrolyte}/\text{V}_2\text{O}_5$) and hybrid device ($\text{Li}_x[\text{Nb}_2\text{O}_5+\text{PEDOT:PSS}]/\text{electrolyte}/[\text{V}_2\text{O}_5+\text{PEDOT:PSS}]$), (b) the *in-situ* modulation reflectance of the inorganic device ($\text{Li}_x\text{Nb}_2\text{O}_5/\text{electrolyte}/\text{V}_2\text{O}_5$) and hybrid device ($\text{Li}_x[\text{Nb}_2\text{O}_5+\text{PEDOT:PSS}]/\text{electrolyte}/[\text{V}_2\text{O}_5+\text{PEDOT:PSS}]$).

The cyclic voltammograms (CVs) of the ($\text{Li}_x[\text{Nb}_2\text{O}_5+\text{PEDOT:PSS}]/\text{electrolyte}/[\text{V}_2\text{O}_5+\text{PEDOT:PSS}]$) taken between -0.7 V and 0.8 V, at a cycling rate of 10 mV s^{-1} (Figure 7a) illustrates a well reversible behavior with good cyclability associated with nice color switches which differ on the two faces. $\text{Nb}_2\text{O}_5+\text{PEDOT:PSS}$ reversibly changed from blue-white to dark-blue and $\text{V}_2\text{O}_5+\text{PEDOT:PSS}$ from orange to blue/green (Figure 7b).

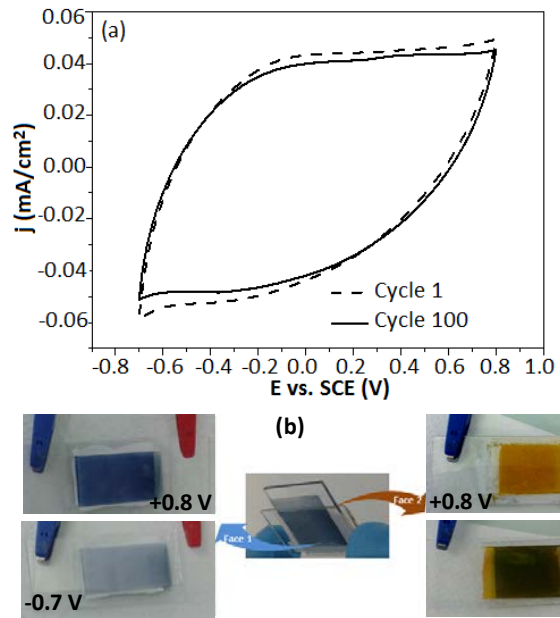


FIGURE 7. Cyclic voltammograms of the ITO/ $\text{Li}_x[\text{Nb}_2\text{O}_5+\text{PEDOT:PSS}]/\text{electrolyte}/[\text{V}_2\text{O}_5+\text{PEDOT:PSS}]/\text{ITO}$ hybrid device between -0.7 and 0.8 V with a 10 mV/s scan rate for 100 cycles (a). Schematic of ITO/ $\text{Li}_x[\text{Nb}_2\text{O}_5+\text{PEDOT:PSS}]/\text{electrolyte}/[\text{V}_2\text{O}_5+\text{PEDOT:PSS}]/\text{ITO}$ electrochromic device combining $\text{Li}_x[\text{Nb}_2\text{O}_5+\text{PEDOT:PSS}]$ and $\text{V}_2\text{O}_5+\text{PEDOT:PSS}$ films on ITO substrates separated by an electrolyte membrane consisting of LiTFSI–BMITFSI mixture with TiO_2 and blended with PMMA (b).

The switching kinetics of the hybrid device was investigated by chronoamperometric (CA) measurements. Figure 8 shows current transient ($j-t$) for the ITO/ $\text{Nb}_2\text{O}_5+\text{PEDOT:PSS}/\text{LiTFSI-EMITFSI}+\text{TiO}_2$ in PMMA / $\text{V}_2\text{O}_5+\text{PEDOT:PSS}/\text{ITO}$ for potential steps of ($+1 \text{ V}/30 \text{ s}$) and ($-1 \text{ V}/30 \text{ s}$). Both response times are in the order of a few seconds; 3 s for the oxidation and 2 s for the reduction.

The optical contrasts of the two faces were evaluated using the $L^*a^*b^*$ color system. In fact, in CIE colorimetric space, the color is represented by three parameters: a luminance axis (L^*) and two hue axes (a^*) and (b^*), which can be used to define and compare quantitatively the colors. The optical contrast ΔE^* is defined by this equation:

$$\Delta E^* = [(L^*_c - L^*_b)^2 + (a^*_c - a^*_b)^2 + (b^*_c - b^*_b)^2]^{1/2}$$

For both sides $\text{Nb}_2\text{O}_5+\text{PEDOT:PSS}$ switch from white-blue to dark-blue, and $\text{V}_2\text{O}_5/\text{PEDOT:PSS}$, from orange to green-blue, are in the order of 55 and 46, respectively.

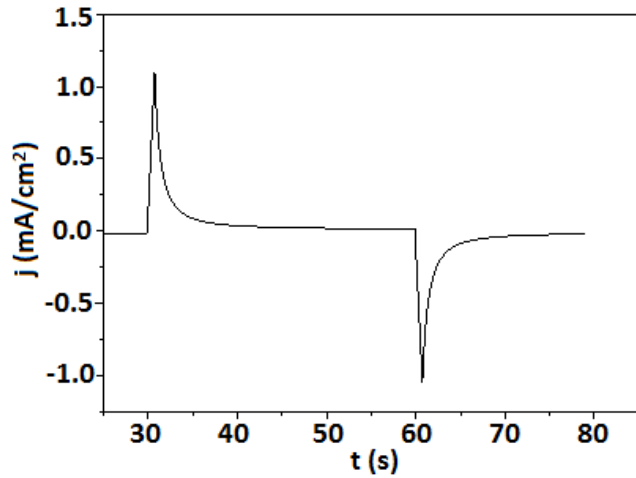


FIGURE 8. Chronoamperograms of $\text{Li}_x[\text{Nb}_2\text{O}_5 + \text{PEDOT:PSS}]/\text{electrolyte}/[\text{V}_2\text{O}_5 + \text{PEDOT:PSS}]$ device at -1 V for 30 s and 1 V for 30 s.

Figure 9 shows the *in-situ* optical reflectance spectra for the bleached and colored states from the double sided hybrid EC device at wavelengths ranging from 300 to 800 nm. The reduced blue-white state (-1 V/30 s) and the oxidized dark blue state ($+1$ V/30 s) (**Figure 9a**) are associated with reflectance values of about $R_R \approx 16\%$ and $R_O \approx 60\%$ at 550 nm, respectively, corresponding to a reflectance modulation ΔR of 44%. The *in-situ* evolution of the reflectance spectra for the second hybrid face ($\text{V}_2\text{O}_5 + \text{PEDOT:PSS}$) is depicted in (**Figure 9b**). The reduced-green state (-1 V/30 s) and the oxidized-orange state at ($+1$ /30 s) are associated with reflectance values of about $R_R \approx 3\%$ and $R_O \approx 26\%$ at 550 nm, respectively, with a total reflectance modulation of $\Delta R \approx 23\%$.

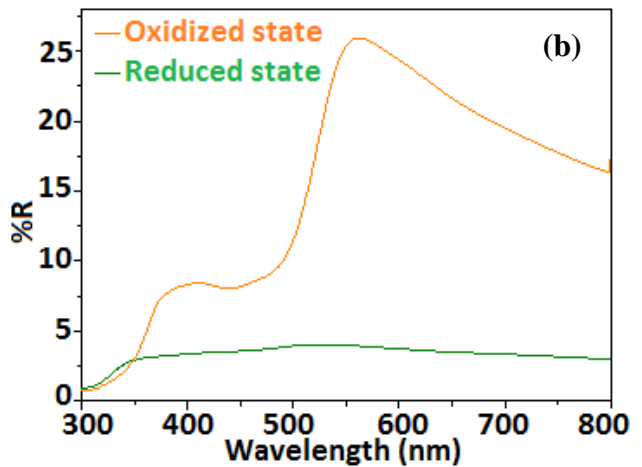
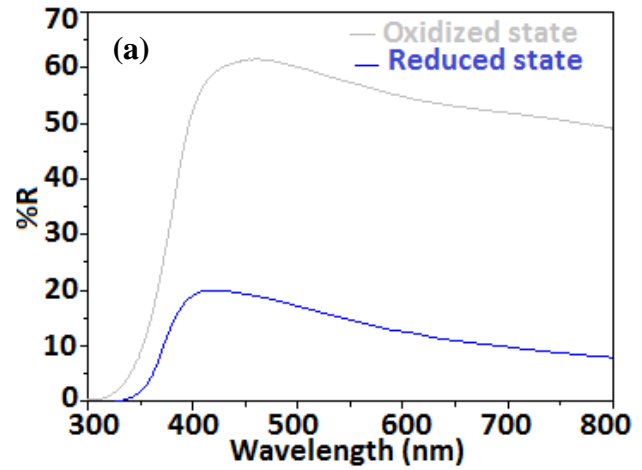


FIGURE 9. *In-situ* diffuse reflectance spectra of $\text{Li}_x[\text{Nb}_2\text{O}_5 + \text{PEDOT:PSS}]/\text{electrolyte}/[\text{V}_2\text{O}_5 + \text{PEDOT:PSS}]$ device at -1 V for 30 s and 1 V for 30 s (a) face based niobium and (b) face based vanadium.

IV. Conclusion

In summary, hexagonal nano- Nb_2O_5 was synthesized by facile and low-cost method, namely the polyol process. Nb_2O_5 electrochromic thin films were successfully deposited on ITO substrate at room temperature by Dip-Coating. Homogenous Nb_2O_5 films show nice electrochromic properties switching reversibly from white to blue color when cycled in lithium based ionic liquid electrolyte. Improvement of the electrochromic properties of Nb_2O_5 was achieved by mixing with PEDOT-PSS prior to the fabrication of a novel double-sided device built from $\text{Li}_x[\text{Nb}_2\text{O}_5 + \text{PEDOT:PSS}]/\text{electrolyte}/[\text{V}_2\text{O}_5 + \text{PEDOT:PSS}]$ assembly. This double-sided electrochromic device exhibited nice optical contrast and fast color switching opening applications in the decorative field for instance.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Detailed description of the Full-pattern matching using isotropic peak profile function of the niobium pentoxide powders synthesized by polyol process and the unit-cells parameters and R reliability factors extracted from the pattern matching refinement of Nb₂O₅ powders annealed at 500 °C under air for 2 h. A Detailed description of all the experimental procedures to prepare the two hybrids films prior to their assembly in a double-sided device.

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The manuscript was written through contributions of all authors.

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ABBREVIATIONS

EC, electrochromic

ECD, electrochromic device

CE, coloration efficiency

ΔE*, optical contrast

(LiTFSI), lithium trifluoromethanesulfonimide.

(EMITFSI), 1-ethyl-3-methylimidazolium bis (trifluoromethanesulfonyl) imide.

PEDOT:PSS, poly(ethylene-3,4-dioxythiophene): poly (styrenesulfonic acid)).

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TOC

