Spectroscopic, morphological and electrochromic characterization of layer-by-layer hybrid films of polyaniline and hexaniobate nanoscrolls
Spectroscopic, morphological and electrochromic characterization of layer-by-layer hybrid films of polyaniline and hexaniobate nanoscrolls†

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The combination of semiconducting oxides and polyaniline in the nanoscale range may result in hybrid materials with enhanced properties, such as electrochromism and charge capacity. This paper reports the spectroscopic, morphological and electrochromic characterization of hybrid films made up of hexaniobate one-dimensional (1D) nanoscrolls and polyaniline prepared by the layer-by-layer assembly technique (LbL). Secondary electron imaging and backscattered electron imaging techniques performed using a scanning electron microscope showed that polyaniline is adsorbed on the hexaniobate nanoscrolls, which confirms the combination of the components in the nanoscale domain. UV-VIS-NIR electronic spectra of the LbL hybrid films showed the absorption tail in the NIR region, assigned to delocalized polarons of the polyaniline. Resonance Raman spectra in the 1000–1700 cm⁻¹ range indicated that hybrid films present a higher relative intensity of polaron bands at 1337 and 1508 cm⁻¹ than pristine polyaniline in the emeraldine salt form. These results suggest that hexaniobate nanoscrolls induce a secondary doping of polyaniline. The cyclic voltammetry (CV) data for the hybrid film showed a specific capacity of 870 C cm⁻². According to CV results, the synergistic effect on charge storage properties of the hybrid material is attributed to the enhanced electroactivity of the hexaniobate component in the LbL film. Spectroelectrochemical experiments showed that the electrochromic efficiencies at 420 nm are ca. -41 and 24 cm² C⁻¹ as the potential changes from 0.8 to -0.9 V and from -0.9 to -1.8 V, respectively, whereas at 800 nm the efficiencies are ca. -55 and 8 cm² C⁻¹ for the same potential ranges. The electrochromic efficiencies and multi-colour character of the LbL film of hexaniobate nanoscrolls and polyaniline indicate that this novel hybrid material is an interesting modified electrode for electrochromic devices.

1. Introduction

Some materials containing semiconducting oxides, conducting polymers or metallopolymers present interesting electrochromic properties, i.e., their optical properties are changed when a small variation in the electric potential is applied.¹-³ Electrochromic films can be used in commercial and residential windows, decreasing the thermal discomfort and the energy consumption in buildings.¹ The operation of electrochromic devices based on semiconducting oxides depends on the reversible electrochemical reduction–oxidation of the transition metal by the insertion–deinsertion of positive ions and electrons into the oxide structure.

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Exfoliation of hexaniobate is achieved by decreasing the electrostatic interaction between the interlayer cations and the negative layers, and stabilization of the dispersed nanosheets. The intercalation of n-alkyl amines or tetra(n-alkyl)ammonium species is an efficient strategy of exfoliation.\textsuperscript{12,16–22} In addition, many authors have reported that the exfoliation of hexaniobate (NbO) with tetra(n-butyl)ammonium hydroxide (TBAOH) promotes the curling of the exfoliated nanosheets, resulting in 1D metal oxide nanoparticles known as hexaniobate nanoscrolls (NbONsc).\textsuperscript{16,17,22–24} The processes of hexaniobate exfoliation and formation of NbONsc are simplified and shown in Scheme 1. Although the mechanisms of the nanosheets curling and the nanoscrolls stabilization are not well elucidated, NbONsc have been used to produce hybrid materials for photo-production of H\textsubscript{2} and O\textsubscript{2},\textsuperscript{17,21,24} and for encapsulation of magnetic nanoparticles.\textsuperscript{25} It is important to emphasize that niobate nanoparticles are produced by soft chemical routes and show flexibility, transparency, high aspect ratios and chemical stability in a large range of pH.

As was mentioned above, conducting organic polymers can display interesting electrochromic properties. In this way, polyaniline deserves to be highlighted since it shows significant application in electronic devices such as electrochromic devices,\textsuperscript{26–28} sensors\textsuperscript{29–32} and batteries.\textsuperscript{33–35} PANI is quite easily processable, low cost and shows environmental stability.\textsuperscript{36} The emeraldine base form of polyaniline (PANI-EB) is equally constituted by reduced and oxidized segments (Scheme 2).\textsuperscript{36–40} The acid doping of PANI-EB results in the conducting form of polyaniline, the emeraldine salt (PANI-ES), as shown in Scheme 2. The high increase in the electrical properties after doping process is attributed to the presence of polaron, formation of which is through an internal redox reaction from a paired spin (bipolarons) to unpaired spin structures (Scheme 2).\textsuperscript{38–41} Conformational changes of the polymer backbone may induce the organization of the polymeric chains, giving rise to free charge carriers and resulting in the improvement of the electrical properties of PANI. This concept is called secondary doping and was applied to polyaniline for the first time by MacDiarmid and Epstein.\textsuperscript{42,43}

Combining together the unique properties of electrochromic materials such as metal oxides and conducting polymers may result in organic–inorganic hybrid nanomaterials with enhanced or novel properties not yet observed for the isolated components.\textsuperscript{44–49} Hybrid electrochromic films based on NiO and polyaniline (PANI) have shown fast operation, high stability and a remarkable efficiency of 85 cm\textsuperscript{2} C\textsuperscript{−1}.\textsuperscript{50}

Considering the design of an electrochromic film consisting of niobium oxide and PANI, we expect that the presence of the

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![Scheme 1](image1.png)  
**Scheme 1** Scheme of the exfoliation process of layered hexaniobate in TBAOH solution and the curling process of the nanosheets resulting in hexaniobate nanoscrolls (NbONsc).

![Scheme 2](image2.png)  
**Scheme 2** Scheme of the doping process of PANI-EB and conversion of bipolarons to polaron in PANI-ES. The anions are not shown (adapted from ref. 38 and 39).
inorganic counterpart as 1D or 2D nanoparticles improves the device response decreasing the ions diffusion path and time.

The design of electrochromic hybrid films should also contemplate a simple method for the device assembly. In comparison to processes such as evaporation, electrodeposition and sputtering, an easy and low-cost procedure for hybrid films preparation is the electrostatic Layer-by-Layer (LbL) assembly technique. This method consists of the alternate deposition of polycation and polyanion layers on a solid substrate.\textsuperscript{55–57} In addition to the simplicity of the preparation and the thickness control of the films, the most important advantage of the LbL technique is to enable the thorough interpenetration of polycation–polyanion layers. This feature gives rise to an improved interaction between polycation and polyanion, which may result in superior properties by the secondary doping of PANI and the enhancement of the electrochromic response.\textsuperscript{55–57}

This paper reports the spectroscopic, morphological and electrochromic characterization of organic–inorganic hybrid films of the two electrochromic species hexaniobate nanoscrolls (anionic) and polyaniline (cationic) by the simple LbL technique. The combination of the organic–inorganic counterparts in the nanoscale domain promoted the high doping level of polyaniline and, consequently, the attainment of hybrid film with prominent electrochromic efficiencies and multi-colour character. This novel hybrid material is an interesting modified electrode for electrochromic devices.

2. Experimental section

2.1. Preparation of polyanilines and dispersion of emeraldine salt polyaniline (PANI-ES)

PANI-ES was prepared following the usual chemical oxidative polymerization of aniline with ammonium peroxysulfate in 1 mol L\textsuperscript{−1} hydrochloric acid.\textsuperscript{36} PANI-EB was prepared by deprotonation of PANI-ES in 0.1 mol L\textsuperscript{−1} NH\textsubscript{3} solution.\textsuperscript{36} PANI-ES dispersion (pH 2.5) in water–\textit{N},\textit{N}-dimethylacetamide (9/1 in volume) was prepared following the procedure described in the literature.\textsuperscript{54,55}

2.2. Syntheses of hexaniobate and colloidal dispersion of hexaniobate nanoscrolls

The potassium precursor form (K\textsubscript{4}Nb\textsubscript{6}O\textsubscript{17}) was prepared by the ceramic method, heating stoichiometric mixture of Nb\textsubscript{2}O\textsubscript{5} and K\textsubscript{2}CO\textsubscript{3} at 1100 °C for 10 hours.\textsuperscript{14,15} The hydrous phase of K\textsubscript{4}Nb\textsubscript{6}O\textsubscript{17} was confirmed by X-ray diffractometry (XRD) data (\textit{d}040 peak at 9.3 Å). The acid form of hexaniobate (H\textsubscript{4}K\textsubscript{2}Nb\textsubscript{6}O\textsubscript{17}) was prepared by ion-exchange reaction of K\textsubscript{4}Nb\textsubscript{6}O\textsubscript{17} with 6 mol L\textsuperscript{−1} HNO\textsubscript{3} solution (reflux at 60 °C for 6 days).\textsuperscript{58,59} The phase H\textsubscript{2}K\textsubscript{2}Nb\textsubscript{6}O\textsubscript{17}–H\textsubscript{2}O was confirmed by thermogravimetric analysis and XRD data (\textit{d}040 peak at 7.9 Å). Colloidal dispersion of hexaniobate nanoscrolls (NbONsc) was prepared by exfoliation of H\textsubscript{2}K\textsubscript{2}Nb\textsubscript{6}O\textsubscript{17} in solution of TBAOH using TBA\textsuperscript{+}/H\textsuperscript{+}–hexaniobate molar ratio equal to 0.75, according to Shiguihara \textit{et al.}\textsuperscript{19,20} Detailed experimental procedures are available in the ESI\textsuperscript{†}.

2.3. Preparation of layer-by-layer films of hexaniobate nanoscrolls and polyaniline

Glass slides (2.5 cm × 1 cm) were cleaned according to procedures described in the literature,\textsuperscript{52,55} and used as substrates for deposition of LbL films of polyaniline (cationic species) and hexaniobate nanoscrolls (NbONsc, anionic species). The deposition of one bilayer of PANI–NbONsc was carried out as follows (see Scheme 3): glass substrate was (1) dipped in PANI-ES dispersion (pH 2.5) for 3 minutes, (2) rinsed with deionized water by dipping, (3) dipped in 1 mol L\textsuperscript{−1} HCl solution for 30 seconds and (4) dried with N\textsubscript{2} stream; glass substrate was (5) dipped in colloidal dispersion of NbONsc for 3 minutes, (6) rinsed with deionized water by dipping, (7) dipped in 1 mol L\textsuperscript{−1} HCl solution for 30 seconds and finally (8) dried with N\textsubscript{2} stream. This procedure was repeated for 15 times to produce LbL films of 15 PANI–NbONsc bilayers. For spectroelectrochemical experiments, LbL hybrid films of PANI–NbONsc were also prepared using fluorine-doped tin-oxide (FTO) as the substrate (in this case, 15 PANI–NbONsc bilayers were also deposited). For comparison purposes, films containing only NbONsc (without PANI) were prepared by casting on glass or FTO substrates (called as “casting film of NbONsc”).

2.4. Characterization

UV-VIS-NIR electronic absorption spectra were obtained using a Shimadzu UVPC-3101 scanning spectrometer by subtracting

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\[ \text{Scheme 3} \] Scheme for preparation of one bilayer of PANI–NbONsc (starting at number 1). The LbL film of PANI–NbONsc was prepared by repeating the step sequence 15 times. NbONsc = hexaniobate nanoscrolls.
the spectrum of glass substrate. Resonance Raman (RR) spectra were recorded at 632.8 nm excitation radiation (He–Ne laser, Renishaw 7N1753) in a Renishaw Raman imaging microscope (inVia) with a Leica microscope and a CCD detector. Samples were focused by a 50× lens and the laser power was kept below 50 μW to avoid sample photodegradation.

The morphological characterization of the NbONsc was performed for the sample prepared by deposition of the colloidal dispersion of NbONsc on an aluminum stub. Secondary electron images (SEI) of the NbONsc sample were recorded in a Field Emission Scanning Electron Microscope (FE-SEM, JEOL JSM-7410) from Central Análítica do Instituto de Química – Universidade de São Paulo (CA-IQUSP), using an acceleration voltage of 2 kV. SEI and backscattered electron images (BEI) of the LbL film of PANI–NbONsc were recorded on a FE-SEM (JEOL JMS-6701F) from Central Experimental Multiusuário da Universidade Federal do ABC (CEM-UFABC), using an acceleration voltage of 5 kV. The LbL film of PANI–NbONsc deposited on the glass substrate was attached on an aluminum stub by a double-sided copper tape.

For the electrochemical and spectrophotological experiments, a platinum sheet with an area of 10 cm² and Ag/Ag⁺ saturated in propylene carbonate (PC) were used as counter electrode and quasi-reference electrode, respectively. This quasi-reference electrode has a potential of 2.94 V versus Li/Li+. A LiClO₄–PC electrolytic solution (0.5 mol L⁻¹) was utilized in all the electrochemical experiments, which were carried out using an Autolab PGSTAT30 potentiostat/galvanostat. Chromogenic analysis was performed concomitant with the electrochemical experiments using a USB4000 spectrophotometer (Ocean Optics Inc) equipped with an LS1 tungsten halogen light source and fiber optic cables with a diameter of 600 μm. The LbL film of PANI–NbONsc or the casting film of NbONsc was used as the working electrode and placed in a cell made of optical glass, where light beams were transmitted across the sample.

Film thickness was measured by specular reflectance using the Nanocalc 2000 program coupled with a single channel 2048 pixel CCD spectrophotometer with a halogen lamp as the light source. The thickness values measured for the LbL film of PANI–NbONsc (15 PANI–NbONsc bilayers deposited on the glass substrate) and also for the casting film of NbONsc were 90 ± 4 nm and 200 ± 4 nm, respectively.

3. Results and discussion

The quality of the LbL film of PANI–NbONsc and the doping level of polyaniline in the hybrid material were monitored by UV-VIS-NIR electronic spectroscopy. Fig. 1A shows absorption spectra of the LbL hybrid film as function of the number of PANI–NbONsc bilayers. The broad absorption band at 980 nm as a function of the number of PANI–NbONsc bilayers. The linear growth of absorbance indicates that the deposition of polyaniline is reproducible for each bilayer, confirming the proper preparation of a multilayered film of hexaniobate and polyaniline by the layer-by-layer assembly technique.

Fig. 1B shows the RR spectra of the LbL film of PANI–NbONsc and PANI-ES in the 1700–1000 cm⁻¹ range. The bands at 1622, 1586, 1508, 1337, 1259 and 1171 cm⁻¹ can be associated with the polaron bands of PANI-ES at 1619, 1593, 1503, 1355, 1243 and 1161 cm⁻¹, respectively. These bands are characteristic of localized polaron bands of PANI-ES at 1619, 1593, 1503, 1355, 1243 and 1161 cm⁻¹. The RR spectrum of the hybrid film presents characteristic bands assigned to the doped form of polyaniline, according to results of UV-VIS-NIR spectroscopy (Fig. 1). Considering that hexaniobate presents strong bands below 1000 cm⁻¹ (ref. 67 and 68) and also is not in resonance Raman condition using the 632.8 nm excitation radiation, all the spectral features in the 1700–1000 cm⁻¹ range are exclusively due to polyaniline in the hybrid film.
formation of cross-linking segments could be induced by the photoactivity of hexaniobate in the hybrid film. It has been reported that hexaniobate is a catalyst for light-induced decomposition of acid red G due to the formation of reactive species, such as OH radicals. Fig. 2B shows the expanded and amplified spectra of the LbL film of PANI–NbONsc and PANI-ES in the 1560–1440 cm⁻¹ spectral range. The fitted Gaussian band centered at 1510 cm⁻¹ is assigned to the βN–H vibration modes of polarons (1512 cm⁻¹ for pristine PANI-ES), while the band centered at 1486 cm⁻¹ is assigned to the ρC–C of bipolarons (1483 cm⁻¹). According to Fig. 2B, the intensity ratio of the Raman bands (1510 cm⁻¹/1486 cm⁻¹) in the LbL film PANI–NbONsc is higher than that observed for PANI-ES (1512 cm⁻¹/1483 cm⁻¹). The higher relative intensity of the polaron band in the hybrid film indicates the higher conversion of bipolarons to polarons (Scheme 2), due to conformational changes of polyaniline (secondary doping). These conformational modifications could be promoted by the strong electrostatic interaction between protonated PANI and the negative niobate particles, and also by hydrogen bonding interactions. The high surface area of nanoparticles can also contribute to enhance the interaction with the polymer. These results are in accordance with UV-VIS-NIR spectroscopy data (Fig. 1) and with the literature, which have shown that secondary doping of polyaniline could be induced when assembled in LbL films.

Morphological characterization of the hybrid film was performed by the scanning electron microscopy (SEM) technique, with acquisition of secondary electron (SEI) and backscattered electron (BEI). The SEI image of NbONsc without PANI (Fig. 3) confirms that exfoliation of hexaniobate with TBAOH yields a material of homogeneous morphology of nanoscrolls. The mean diameter of the NbONsc considering over one thousand nanostructures from additional images is ca. 26 ± 5 nm (see ESI†). This value is consistent with reports in the literature. Although the preparation of NbONsc is well established in the literature, morphological characterization of such nanostructures has been performed only by transmission electron and atomic force microscopies. To our knowledge, this is the first report of SEI images of hexaniobate nanoscrolls. Comparing the SEI image of the LbL film of PANI–NbONsc in Fig. 4 to that of NbONsc without PANI (Fig. 3), it is observed that the former presents higher surface roughness on nanostructures. This roughness is associated with the presence of polyaniline adsorbed on the NbONsc, forming a hybrid nanomaterial. The BEI technique presents higher contrast mostly due to domains with high local mean atomic number. Therefore, the

![Fig. 2](image-url) (A) Resonance Raman spectra of PANI-ES and hybrid LbL film of PANI–NbONsc and (B) peak fitting of Raman bands at 1560–1440 cm⁻¹ (dashed lines).

![Fig. 3](image-url) SEI image of NbONsc sample prepared by deposition on Al stub. The mean diameter of the NbONsc considering over one thousand nanostructures is ca. 26 ± 5 nm (see additional images in the ESI†).
BEI image of the LbL hybrid film of PANI–NbONsc may present higher contrast due to the NbONsc component (higher mean atomic number compared to polyaniline). In Fig. 4, it can be seen that the BEI image clearly identifies nanostructures of high aspect ratio in the same regions of the nanoscrolls seen in the SEI image. The highlighted regions in Fig. 4 show the differences between SEI and BEI images, whereas the surface roughness due to PANI in the LbL film is only observed in the upper image.

Fig. 5A shows the UV-VIS electronic absorption spectra of the casting film of NbONsc and the LbL hybrid film of PANI–NbONsc on glass substrates. Absorbance changes of the (B) LbL film of PANI–NbONsc and (C) casting film of NbONsc on the FTO substrate at different potentials (vs. Ag/Ag⁺).

In order to investigate the absorbance changes in the LbL film of PANI–NbONsc and the casting film of NbONsc for different oxidation states, the materials were prepared on FTO substrates. Fig. 5B displays the absorbance changes (∆A) for the LbL film of PANI–NbONsc at 0.8, −0.8, −1.1, and −1.8 V vs. Ag/Ag⁺. The values of ∆A decrease from 0.8 to −0.8 V, which indicates the decrease of polaron population associated with PANI electro-reduction during the lithium ion electro-insertion. Meanwhile, the absorbance change increases at more negative potentials due to reduction of Nb(v) to Nb(IV). In fact, this is also observed for the casting film of NbONsc in Fig. 5C, which shows the increase of absorbance associated with the charge transfer transition and of absorbance background at higher wavelengths for the LbL film in comparison to the casting film of NbONsc.

Fig. 4  SEI and BEI images of the LbL film of PANI–NbONsc. The highlighted regions show the differences between SEI and BEI images, whereas the surface roughness due to PANI in the LbL hybrid film is only observed in the upper image.
Fig. 6A displays the cyclic voltammograms (CV) of the casting film of NbONsc and the LbL film of PANI–NbONsc on FTO substrates. Lithium ion electro-insertion is depicted in the negative potential scan, whereas the ionic electro-deinsertion process is observed during the positive potential scan of these CV. The voltammatic peaks at ca. 0.22 and −0.77 V are associated with PANI reduction, whereas the peak currents at ca. −1.45 V correspond to the reduction from Nb(v) to Nb(iv) during the negative potential scan. These distinct potential ranges corresponding to the participation of PANI and hexaniobate in the electrochemical processes are also seen during the positive potential scan. The voltammatic peaks at −0.82 and 0.33 V correspond mostly to the oxidation of hexaniobate and PANI components in the LbL film, respectively.

The electro-inserted charge (q) in the LbL film of PANI–NbONsc was ca. 7.8 mC cm\(^{-2}\). Considering a thickness of ca. 90 nm, the specific capacity of the hybrid film is ca. 870 C cm\(^{-2}\). According to the literature,\(^\text{34}\) PANI films present a specific capacity close to 770 C cm\(^{-2}\), and the casting film of NbONsc presents a low electroactivity, as can be seen in Fig. 6A (dashed line). Probably, the low current observed for NbONsc at potentials more negative than −1.5 V is associated with the lithium ion electro-insertion and the reductive decomposition of the electrolytic solution on the modified electrode surface.

Therefore, the results reported here indicate that the LbL film of PANI–NbONsc presents enhanced charge storage properties comparing to films constituted only by PANI or hexaniobate, and this synergistic effect is not related to the improvement of the charge capacity of PANI, but is attributed to the enhanced electroactivity of the hexaniobate component in the hybrid nanomaterial. The conducting polymer contributes with 0.69 mC cm\(^{-2}\) of total charge in the LbL film, which corresponds only to ca. 9% (76 mC cm\(^{-2}\)) of the total specific capacity. These results suggest that the Nb(v) sites are more accessible to the lithium ions in the nanomaterial matrix than in the casting film of NbONsc. Besides, PANI chains can improve the connectivity among the NbONsc nanoparticles and, consequently, increase the electronic conductivity.

Fig. 6B shows the values of ΔA as a function of potential for the LbL film of PANI–NbONsc, which were obtained during the CV under monochromatic radiation at 420 and 800 nm. The absorbance changes decrease at −0.95 V and increase at more negative potentials for both wavelengths during the lithium ion electro-insertion. Meanwhile, the absorbance changes reach minimum values at ca. −0.05 V and increase at more positive potentials during the reverse process. These data indicate that the voltammatic reduction peaks at 0.22 and −0.77 V are associated with the reduction from emeraldine salt to leucoemeraldine state, and the voltammatic oxidation peak at 0.33 V corresponds mostly to oxidation from leucoemeraldine to emeraldine salt state, once the difference of absorbance change at 0.8 V after the voltammetric reduction (PANI reduction) and from 0.9 to 1.8 V (hexaniobate reduction), respectively. Meanwhile, the values of ΔA associated with polaron population decrease (increase) during the negative (positive) potential scan.\(^\text{75}\) This potential difference between the voltammatic reduction peaks for PANI can be due to the hindrance conferred by the lithium ion to PANI sites or to the secondary doping due to the presence of hexaniobate nanoscrolls in the hybrid film. Although the lithium ions access these PANI sites at distinct potential ranges, both are oxidized at potentials more positive than −0.05 V, as can be seen by the potentiodynamic profiles of current and absorbance change (Fig. 6A and B). Moreover, it is also important to mention that there is still a small oxidation charge associated with hexaniobate at potentials between −0.05 and 0.8 V (1.03 mC cm\(^{-2}\)), once the oxidation charge at this potential range is higher than the charge associated with the reduction of PANI between 0.8 and −0.9 V (0.71 mC cm\(^{-2}\)).

The obtained results also indicate that this electrochemical system is chemically reversible, as demonstrated by the small difference of absorbance change at 0.8 V after the voltammatic cycle. This feature is very important for application in electrochromic devices. Moreover, this hybrid material is multi-coloured and presents distinct electrochromic efficiency (η) as a function of applied potential. The values of η at 420 nm are ca. −41 and 24 cm\(^{2}\)C\(^{-1}\) as the potential varies from 0.8 to −0.9 V (PANI reduction) and from −0.9 to −1.8 V (hexaniobate reduction), respectively. Meanwhile, the values of η at 800 nm correspond to ca. −55 and 8 cm\(^{2}\)C\(^{-1}\) for the same potential ranges mentioned above. These electrochromic efficiencies are higher than PANI and similar to those observed for other electrodes of PANI with secondary doping in non-aqueous medium.\(^\text{76}\) On the other hand, the values of η at a wavelength (470 nm) of maximum absorbance change for the LbL film of poly(allylamine) and hexaniobate\(^\text{13}\) were slightly higher (ca. 65 cm\(^{2}\)C\(^{-1}\)) than those observed in this paper. However, the LbL...
film of PANI-NbONSc is an alternative modified electrode for electrochromic devices, once this electrochemical system presents higher electrochromic efficiency (in comparison to other electrochromic electrodes, containing WO₃, for instance ref. 77) and covers a wider range in the visible region of the electromagnetic spectrum.

The electrochromic properties of the hybrid films reported here make them suitable for use as primary electrodes in electrochromic devices formed from secondary electrodes of complementary optical properties, such as V₂O₅. This reduced (oxidized) metal oxide absorbs in a similar wavelength range to the oxidized (reduced) LbL film of polyaniline and hexaniobate nanoscrolls. Therefore, we could envisage even more efficient electrochromic devices due to these complementary properties.

4. Conclusions

Hybrid films of hexaniobate nanoscrolls and polyaniline were prepared by the ease and low-cost layer-by-layer assembly technique. Morphological characterization of the LbL film showed that polyaniline is adsorbed on the hexaniobate nanoscrolls, which confirms the combination of the components in the nanoscale range. To our knowledge, this is the first report of hexaniobate nanoscrolls observed by scanning electron microscopy. Spectroscopic data showed that polyaniline is secondarily doped in the LbL film, probably induced and optimized by the strong electrostatic interaction and hydrogen bonding with the 1D hexaniobate nanoparticles. The combination of the components in the nanoscale range and the higher doping level of polyaniline compared to pristine polymer resulted in a hybrid material of higher electrochromic efficiencies and multi-colour character (41 and ~55 cm² C⁻¹ for 420 and 800 nm, respectively), and higher specific capacity (870 C cm⁻²). This novel nanomaterial is an interesting modified electrode for electrochromic devices.

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