A new hybrid electrochromic material: vanadium oxide/eriochrome black T

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Abstract. In this work, we describe the synthesis of a new hybrid material, which is consists of the eriochrome black T (sodium 1-[(1-hydroxynaphthalen-2-yl-hydrazinylidene]-6-nitro-2-naphthol-4-sulfonate) and vanadium pentoxide xerogel using a melting sonoquenching technique. This hybrid material was apply in electrochromic electrodes. The hybrid material was characterized by X-ray difraction, FT-IR, AFM and spectroelectrochemically. The hybrid presented good reversibility and cyclability during 50 cycles studied, electrochromic efficiencies were about 50 cm² C⁻¹ (375 nm and 400 nm) and the ∆OD at 375 nm and 400 nm were 0.236 and 0.159 respectively wavelengths. The response times were 0.7 to 3.3 s for 375 nm and 0.7 to 2.0 s for 400 nm. The hybrid is a potential material to be used in electrochromic applications.

1. Introduction

Vanadium oxide has been studied due its several applications such as secondary batteries and as electrochromic material [1-3]. Among them the electrochromic property draws attention and stands out since it can change its colour due an external application of potential.

Studies show that yellow vanadium oxides films can be converted into green or blue when applying a potential. This colour change is related to a insertion/extracting of ions and electrons from the $V_2O_5$ structure, creating species with the $M\cdot V_2O_5$ formula (where $M^+$ represents ions, such as Li⁺ and H⁺), and the response of these films are related to some parameters as its crystallinity, degree of disorder and morphology [4-6].

Vanadium oxide has many possible structures, and among them it has a layered structured, known as $V_2O_5$ xerogel, that allows the intercalation of other materials. Therefore, $V_2O_5$ xerogel can be classified as an inorganic matrix in which other kinds of materials as organic molecules can be inserted, resulting in an organic-inorganic hybrid material [4,7,8].The new material is interesting because it may have different properties compared with its inorganic matrix, $V_2O_5$ in this case, resulting in a new electrochromic material. These new materials can have different stages of colour, better response times and good transmittance variations on the UV-Vis spectra when applying a potential.

For example, studies showed that the hybrid $V_2O_5$0.07H₂O(C₂H₂₂N₂O₂Br₂)₀.₂₆ can be synthesized by melting sonoquenching technique [4]. Intercalation of carboxybenzylaviologen was increased the interlayer distance of de vanadium oxide matrix in 0.7 Å. It could also be seen that it has a great transmittance variation (92.7%) and it showed good response times, between 6 and 9 seconds, concluding that the hybrid synthesized has a great potential to be applied into electrochromic electrodes.
Another nanostructured hybrid was synthesized by melting sonoquenching technique recently [9], \( \text{V}_2\text{O}_5.1.26\text{H}_2\text{O}([\text{C}_3\text{N}_2(\text{C}_6\text{H}_7\text{N})_3]_{0.07}) \) nanofibers. The organic guest provokes an interlayer spacing decrease of the inorganic matrix and the electrostatic interaction between the oxo groups of the \( \text{V}_2\text{O}_5 \) matrix and the pyridinium rings of the organic guest demonstrate a strong interaction. The new hybrid nanostructure presented good reversibility and cyclability during 50 cycles, electrochromic efficiency of 22 cm\(^2\) C\(^{-1}\) (410 nm) and 96% color retention after 50 cycles of color changing.

In this paper we report the synthesis, using a melting sonoquenching technique, and characterization of an organic-inorganic hybrid, using as inorganic matrix, vanadium oxide as an intercalation material, eriochrome black T (sodium 1-[(1 hydroxynaphthalen-2-yl-hydrazinylidene]-6-nitro-2-naphthol-4-sulfonate) with potential application into electrochromic electrodes.

2. Experimental Procedure

2.1. Synthesis of hybrid material

The powder of \( \text{V}_2\text{O}_5 \) was first put into alumina crucible, then it was calcined in a muffle furnace at 800\(^\circ\)C for one hour and the molten compound (\( \text{V}_2\text{O}_5 \)) was fast poured into water-based saturated solution of the eriochrome black T (sodium 1-[(1-hydroxynaphthalen-2-yl-hydrazinylidene]-6-nitro-2-naphthol-4-sulfonate) into an ultrasonic bath. The mixture was left in ultrasonic bath (Unique model USC1400, 40 kHz and 120 W) for 30 minutes. The wet gels were aged for 7 days at room temperature in sealed test tubes. After aging, the sample was washed several times with ethanol until the upper layer became colorless.

The hybrid material was used to deposit thin films on FTO (fluorine-doped tin oxide coated glass substrate) using spin-coating technique. The spin-coater used is homemade equipment. All parameters (rpm, time, concentration of suspension and applied volume) were the same for all material studies to maintain the same geometric area, uniformity surface and film thickness. For all the depositions, 1,000 rpm, 1 min. and 10 drops of a suspension of the materials (50 mg mL\(^{-1}\) in isopropyl alcohol) were used. The exposed area was 0.84 cm\(^2\) and the resulting electrodes were dried up at 110 \(\circ\)C for 24 h.

An aliquot of the material was dried up at 110 \(\circ\)C for 24 h and the powder of the hybrid material was characterized by X-ray diffraction, FT-IR, AFM and spectroelectrochemically.

2.2. Measurements

X-ray powder diffraction (XRD) data were recorded on a Bruker-AXS D8 Advanced diffractometer using a LynxEye detector and Cu-Ka emission lines (1.541 Å, 40 kV, 40 mA). The diffraction patterns were collected in a flat geometry and data were collected at room temperature over the range 3 \(\leq\) 2\(\theta\) \(\leq\) 85 with steps of 0.02\(^\circ\) and accumulation time of 0.5 s per step.

Fourier transform infrared spectroscopy (FT-IR) measurements were taken in a Varian 660-FTIR spectrometer.

Atomic force microscopy (AFM) was taken in a Nanosurf Flex AFM. The hybrid material was deposited on a Si substrate and images were acquired by tapping mode at room temperature conditions, using a Nanosurf easyScan 2 Flex AFM scanner and cantilever type Tap190Al-G (BudgetSensors).

Spectroelectrochemical measurements were taken using a potentiostat/galvanostat Microautolab Type III and a spectrophotometer Ocean Optics USB650UV. The electrochemical cell consisted of a quartz cuvette with 1 cm optical path containing three electrodes. The working electrode was glass covered with FTO with the hybrid material deposited on a conducting surface using the technique of spin-coating, the counter electrode was a Pt wire and the quasi-reference electrode was a silver wire coated with AgCl. A solution of 0.5 mol L\(^{-1}\) LiClO\(_4\) in acetonitrile was used as electrolyte. The optical and electrochemical measurements were carried out at room temperature.

3. Results and Discussion
XRD measurement of the hybrid material was performed, and is shown in figure 1(a). The XRD pattern indicated the presence of the peak at 2θ = 7.0° for the (001) diffraction plane, as expected for a layered material with parallelism between layers and the reflection plane, corresponding to the interlayer distance of 14.2 Å. It is also observed that in addition to an amorphous phase, there is a crystalline phase of vanadium oxide, it was indexed with V₂O₅ (Shcherbinaite) #96-901-2221, space group Pmn21(31) at orthorhombic crystal system. Another form of characterization was through FT-IR spectroscopy. Figure 1(b) shows the FT-IR spectra for the vanadium oxide in (i), for the eriochrome black T in (ii) and for the hybrid material in (iii). FTIR spectrum of the hybrid shows the presence of some bands that may be related to the organic intercalant present as the band 3406 cm⁻¹ related to νOH (which can also be related to the presence of water) and a band at 1621 cm⁻¹ relating to the C=C bond of the ring overlying the band νH-O-H of water present in the lamellar inorganic matrix. In addition, it can be seen that there are two bands of low intensity in range of 1600-1000 cm⁻¹ (one at 1403 cm⁻¹ and the other at 1098 cm⁻¹) possibly related to ν=C=N in the structure and the νC-C in the ring, respectively. The low intensity of the bands described above is due possibly to the small amount of organic material in the intercalated inorganic hybrid matrix. Moreover, one can notice the presence of the bands at 1006 cm⁻¹ (peeled 13 cm⁻¹ for wavenumbers when compared to V₂O₅) for the ν V=O which, as can be seen by the spectrum had intensity increased compared with the spectrum inorganic matrix, a fact which is possibly overlapping of this band with the band S=O of the intercalant. Also observed a band at 531 cm⁻¹ (10 cm⁻¹ shifted to longer wavelengths compared to V₂O₅) can be attributed to νsym V-O-V. It can also be noted that there is a band at 809 cm⁻¹ which is due to δV-O-V, which was taken off 4 cm⁻¹ to longer wavelengths when compared with V₂O₅. The displacement of these bands is possibly related to hydrogen bonds present in the hybrid in question, amending the interactions of the pyramidal structure of the matrix.

Figure 1. (a) X-ray diffraction of the hybrid material. (b) FT-IR measurements for V₂O₅ in (i), eriochrome black T in (ii) and hybrid material in (iii).

AFM measurements were performed in order to analyze the morphology of the synthesized material. It could be seen that the hybrid has a fibrous structure, as it is shown in figure 2. This structure has approximately 15 nm in width and between 0.4 and 0.6 μm in length.
The spectroelectrochemical characterization of the hybrid synthesized was performed in order to verify its potential to be applied into electrochromic electrodes. Figure 3(a) shows the cyclic voltammogram of the hybrid in a scan rate of 5 mV s\(^{-1}\) in the potential range of -0.6 to 1.2 V (vs Ag/AgCl). Figure 3(a) shows a reversible cyclic voltammogram that exhibits three oxidation peaks at 0.18 V, and 0.65 V (possibly related to the oxidation process of V\(^{4+}\) to V\(^{5+}\)), and at 0.35 V (related to the organic molecule intercalated). Also, three reduction peaks at 0.38V, -0.22V (associated to the reduction of V\(^{5+}\) to V\(^{4+}\)), and at 0.045 V (possibly associated with a reduction that occurs at the organic molecule).

The absorbance spectra of the hybrid under different applied potentials are shown in figure 3(b). The spectra obtained is different from the spectra observed to the V\(_2\)O\(_5\) pure, indicating the synthesis of a new electrochromic material. It can be noted that the UV-Vis spectra showed absorption bands at 327 nm, which is related to \(\pi-\pi^*\) transition, bands at 378 and 462 nm, which are related to charger transfer and a low band at 621 nm related to d-d transitions. It can be noted that during the oxidation process a significant increase in the intensity of absorption of the bands at 327; 378 and 462 nm.

Figure 3. Cyclic voltammogram of the hybrid at 5 mV s\(^{-1}\) in (a) and UV-Vis spectra on chronoamperometry at constant current in (b).
Chronoamperometric analysis (not showing here) was performed by monitoring the optical density variation, at the wavelength 375 and 400 nm, which consisted of applying -0.6 V for 30 seconds and, then, 1.2 V for the same time. A total of 50 cycles were conducted. It was possible to note that the transmittance variation (ΔT%) \textit{in situ}, between the oxidized and reduced states, was 79.5% for 375 nm and 77.4% for 400 nm after 50 cycles, respectively.

It was also possible to calculate the response time. In this work, the response time was defined as the required time to reach 75% of the total of the transmittance variation. The results showed that at 375 nm, the response time was between 0.7 and 3.3 seconds, whereas at 400 nm, it ranged between 0.7 and 2.0 seconds. In addition, other parameters were analysed, such as the electrochromic efficiency, which was about 50 cm$^2$ C$^{-1}$ for both the studied wavelengths and the ΔOD (0.236 at 375 nm and 0.159 at 400 nm).

4. Conclusions

This contribution demonstrates that it is possible to obtain an unprecedented hybrid nanomaterial using the melting sonoequenching techniques. This hybrid, with defined morphology, can be used as electroactive material in electrochromic electrodes. The electrochromic efficiencies were about 50 cm$^2$ C$^{-1}$ (375 nm and 400 nm) and the ΔOD at 375 nm and 400 nm were 0.236 and 0.159, respectively. The response time was 0.7 to 3.3 s for 375 nm and 0.7 to 2.0 s for 400 nm, respectively. From the measurements of FT-IR and XRD, it was possible to conclude that the hybrid vanadium oxide and the eriochrome black T were successfully synthesized, and AFM measurements showed that it has a fibrous structure. In addition, from the spectroelectrochemical measurement, it has different properties from vanadium oxide and that it could be seen that this hybrid is a potential material to be used in electrochromic applications.

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