Graphene-poly(Nickel complex) as novel electrochromic nanocomposite for the fabrication of a robust solid-state device

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ABSTRACT

An electrochromic nanocomposite based on a nickel-*salen* polymeric film - poly[Ni(3-Mesalen)], Mesalen = *N,N'*-bis(3-methylsalicylideneimine) - and graphene nanoplatelets (GFNPs) with enhanced electrochromic stability was successfully prepared by anodic electropolymerization.

Although the electrochemical processes typical of the polymer film were not changed by the presence of graphene, higher electroactive surface coverages could be obtained for nanocomposite films, which suggest the incorporation of GFNPs into the polymeric network. The nanocomposite showed multi-electrochromic behavior, with color changes between yellow (reduced state) and green (oxidized state). The inclusion of GFNPs into the poly[Ni(3-Mesalen)] structure accelerates the switching process, with the response time for green coloration decreasing by 50.7% and for yellow coloration by 60.0%, for films prepared with 30 electropolymerization cycles. In terms of electrochemical stability, after 10 000 electrochemical cycles the loss of charge was 7% for the graphene nanocomposite. The nanocomposite film was used as electrochromic material to assemble a flexible solid-state electrochromic device (ECD), which exhibited an outstanding electrochemical stability - only 3% of charge loss after 15 days of continuous activity.

Keywords: Electrochromism, Metal *salen* complexes, Graphene, Polymeric nanocomposites, Solid-state device.

1. INTRODUCTION

The study of electrochromism, characterized by the reversible color change of an electroactive material as result of its electrochemical oxidation / reduction ^{1,2}, has led to considerable progress in the synthesis of electrochromic materials and optimization of their properties,³⁻⁷ as well as in the manufacture of electrochromic devices (ECDs).^{2,8-13}

Currently, one of the main technological challenges is the development of low cost, flexible and low energy consumption electronic devices for optical information^{1,14}. In this context, conducting polymers have been highlighted as a promising class of electrochromic materials,⁷ although commercial realization of their potential has to date been limited by their durability and switching times.

Graphene has also attracted growing attention as a potential candidate for application in electrochemical and photo-electronic systems.^{15,16} Its two-dimensional structure exhibits a unique band structure and a range of unusual properties, notably very high values of charge carrier mobility ($\approx 200\,000\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$), specific surface area ($\approx 2\,630\text{ m}^2\text{ g}^{-1}$), elastic modulus ($\approx 1\,100\text{ GPa}$), tensile strength ($\approx 125\text{ GPa}$) and thermal conductivity ($\approx 5\,000\text{ W m}^{-1}\text{ K}^{-1}$), together with high chemical stability and optical transmittance.¹⁷⁻²² For these reasons, graphene and its derivatives have been identified as good components for conductive polymer-based composites for technological applications,²³⁻²⁵ since this materials combination results in improvement of electrical conductivity and optoelectronic properties.²⁶⁻²⁸ Although the study of electrochromic graphene-based systems is still in its infancy, recent reports reveal that the incorporation of graphene-derivatives in conductive polymer matrices enhances electronic transport in the polymer, with consequent improvement of response times and coloration efficiency.²⁹⁻³¹ Reddy *et al.* have shown that composite films of PEDOP-wrapped reduced graphene oxide showed 2-fold increase in electronic conductivity and improved switching

kinetics compared with pure PEDOP.²⁹ More recently, Xiong *et al* reported that covalent bonding of polyaniline to functionalized graphene oxide resulted in an increase of optical contrast (from 0.38 to 0.52) and a decrease of bleaching time.³²

In this work, we extend these concepts through the preparation and electrochemical, optical, compositional and morphological characterization of a novel electrochromic system based on a composite of a M-*salen*-type polymer – poly[Ni(3-Mesalen)], with Mesalen = *N,N'*-bis(3-methylsalicylideneimine) – and graphene nanoplatelets; the ultimate goal is assembly of a robust solid-state prototype electrochromic device (ECD). Qualitatively, the pure polymer showed good electrochemical stability and an interesting color change from yellow in the fully reduced state to green and russet in higher oxidation states but, quantitatively, some of the EC properties required improvement for assembly of a practical ECD.³³ Consequently, in the present work, we explore the influence of a conductive nanomaterial – graphene nanoplatelets – on the electrochromic properties of poly[Ni(3-Mesalen)], in pursuit of fabrication of a solid state ECD. We now show that incorporation of graphene nanoplatelets into the poly[Ni(3-Mesalen)] structure significantly improved the EC properties of the pure polymer film, manifested via faster switching times and higher electrochemical stability. This permitted fabrication of an ECD on a flexible substrate (ITO/PET) with only 3% charge loss after 15 days of continuous switching. To the best of our knowledge, this is the first time that the beneficial effect of graphene on electrochromic properties of the Ni-*salen* matrix has been reported and resulted in the fabrication of a small EC prototype.

2. EXPERIMENTAL SECTION

2.1. Materials and Instrumentation

The complex *N,N'*-bis(3-methylsalicylideneimine) nickel(II), [Ni(3-Mesalen)], and corresponding *salen* ligand were prepared as described in the literature.³⁴ Lithium perchlorate (99.9%, Aldrich), hydroxyethyl methacrylate (HEMA, Aldrich) and 2,2-dimethyl-1,3-propanediol (NPG, Aldrich), benzoin methyl ether (BME, Fluka), ethylene carbonate (EC, Huntsman Jeffsol) and acetonitrile and propylene carbonate (PC, Romil, pro analysis grade), synthetic graphite (99.9%, Alfa Aesar) and *N*-2-methylpyrrolidone (NMP, Aldrich) were used as received.

Electrochemical studies were performed using an Autolab PGSTAT 30 potentiostat/galvanostat (EcoChimie B.V.), controlled by GPES software, using a three-electrode cell. The working electrode was indium tin oxide-coated PET (ITO/PET) (Aldrich, resistivity of $60 \Omega \text{ sq}^{-1}$, geometric area of 3.75 cm^2), the counter electrode was a Pt plate (geometric area 2.25 cm^2) and the reference electrode was Ag/AgCl (NaCl / 1.0 mol dm^{-3}) (Metrohm ref. 6.0724.140). In coulometric studies a Pt disk working electrode (geometric area of 0.0314 cm^2 , BAS) was used. Before use the electrode was polished with aluminum oxide (particle size of $0.3 \mu\text{m}$, Buehler) on a microcloth polishing pad (Buehler), then washed with ultra-pure water (resistivity $18.2 \text{ M}\Omega \text{ cm}$, Millipore) and acetonitrile.

The spectroelectrochemical studies were performed *in situ* with a UV-Vis diode array spectrophotometer (Agilent model 8453), coupled to the potentiostat/galvanostat. The experimental set up consisted of a teflon cell with an Ag/AgCl (NaCl / 3.0 mol dm^{-3}) (Bio-Logic) reference electrode, a Pt gauze counter electrode and an ITO/PET (typical area 0.785 cm^2) as working electrode.

X-ray photoelectron spectroscopy (XPS) measurements were performed at Centro de Materiais da Universidade do Porto (CEMUP) (Porto, Portugal), in a VG Scientific ESCALAB 200A spectrometer using non-monochromatised Al $K\alpha$ radiation (1486.6

eV). After Shirley-type background subtraction, the XPS spectra were deconvoluted with the XPSPEAK 4.1 software, using a non-linear least-squares fitting routine. To compensate for errors caused by sample charging, the C1s band at 284.6 eV was used as an internal standard. The surface atom percentages were calculated from the corresponding peak areas, using sensitivity factors provided by the manufacturer. GFNPs were analyzed as pellets and the polymeric films were analyzed as-prepared.

Scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/EDS) analyses were performed at CEMUP (Porto, Portugal) using a high-resolution scanning electron microscope with X-ray microanalysis and backscattered electron diffraction pattern analysis (FEI Quanta 400 FEG ESEM/EDAX Genesis X4M).

Transmission electron microscopy (TEM) analyses were performed at Centro de Investigação em Materiais Cerâmicos e Compósitos (CICECO), Universidade de Aveiro (Aveiro, Portugal), with a Hitachi H-9000NA microscope operating at an accelerating voltage of 200-300 kV. GFNPs were dispersed in ethanol under sonication, after which a carbon-coated 400 mesh copper grid was immersed in the suspension and then air-dried.

2.2 Preparation and characterization of graphene nanoplatelets

GFNPs were prepared by sonication-assisted exfoliation using a titanium ultrasound tip (Bandelin – Sonoplus), according to the procedure described by Khan *et al.*³⁵ Briefly, 10 g of graphite powder was sonicated in 100 mL of NMP for 6 hours. The concentration of the GFNPs was monitored by UV-Vis spectroscopy (at $\lambda = 660$ nm).^{36–38} Then, the dispersion was centrifuged and the supernatant was filtered and dried under vacuum, at room temperature. The resultant GFNPs were characterized by SEM, TEM and XPS; see Supporting Information (SI) (Figures S1, S2 and S3).

2.3 Film preparation and characterization

The deposition solution for the composite films contained 1.0 mmol dm^{-3} [Ni(3-Mesalen)] complex in 0.1 mol dm^{-3} $\text{LiClO}_4/\text{CH}_3\text{CN}$, with 0.5 wt.% of GFNPs (GFNPs/[Ni(3-Mesalen)] wt.%). This solution was refluxed for 3 hours and sonicated for 10 min. GFNPs@poly[Ni(3-Mesalen)] nanocomposite films were electrodeposited by immersing the working electrode (ITO/PET) in this solution and cycling the applied potential between -0.2 and 1.3 V (scan rate, $\nu = 0.1 \text{ V s}^{-1}$; 30 cycles). Pure poly[Ni(3-Mesalen)] films were prepared using the same experimental conditions but without GFNPs in the deposition solution. After electropolymerization, the modified electrodes were thoroughly rinsed with CH_3CN , immersed in 0.1 mol dm^{-3} $\text{LiClO}_4/\text{solvent}$ (CH_3CN or PC, as specified) and cycled in the potential range -0.2 to 1.3 V ($\nu = 0.01 \text{ V s}^{-1}$).

The electroactive surface concentration, $\Gamma / \text{nmol cm}^{-2}$ (cited in terms of monomeric units), of each film was determined by a coulometric assay.³³ Deposition and redox cycling measurements on films prepared with the number of electrodeposition cycles varied in the range 1 to 70 yielded a doping value, n , of 0.65.

The reversible film redox process was monitored by *in situ* UV-Vis spectroscopy during voltammetric cycling (in the potential range -0.2 to 1.3 V; $\nu = 0.02 \text{ V s}^{-1}$), for films immersed in 0.1 mol dm^{-3} LiClO_4/PC . UV-visible spectra (315–1100 nm) were acquired simultaneously at intervals of 0.5 seconds (i.e. 10 mV potential resolution). A background spectrum in 0.1 mol. dm^{-3} LiClO_4/PC was collected for the bare electrode prior to the electropolymerization. Molar extinction coefficients, $\varepsilon / \text{cm}^{-1} \text{ mol}^{-1} \text{ dm}^3$, for each electronic band were determined by combining the Beer-Lambert and Faraday laws:³⁹

$$\text{Abs}(\lambda) = \varepsilon(\lambda)Q / nFA \quad (1)$$

where Q is the charge (C), n is the doping level, F is the Faraday constant and A is the working electrode area (cm^2).

The composition and morphology of reduced GFNPs@poly[Ni(3-Mesalen)] nanocomposite films, were characterized by XPS and SEM/EDS, respectively. The potential was cycled from -0.2 to 1.3 V to -0.2 V ($v = 0.01 \text{ V s}^{-1}$) and the film emerged in the reduced state.

2.4 Electrochromic property evaluation

Film electrochromic properties were studied when exposed to 0.1 mol dm^{-3} LiClO_4/PC . The change in optical density, ΔOD , at a given wavelength, was calculated using:⁴⁰

$$\Delta OD = \log (T_{\text{reduced}} / T_{\text{oxidized}}) \quad (2)$$

where T_{oxidized} and T_{reduced} are, respectively, the film transmittances in the fully oxidized ($E = 1.3 \text{ V}$) and fully reduced ($E = -0.2 \text{ V}$) forms.

The electrochromic contrast, ΔT (the percentage transmittance change at a specific wavelength), was determined using:^{8,41}

$$\Delta T = T_{\text{reduced}} - T_{\text{oxidized}} \quad (3)$$

This was calculated from absorbance values at $\lambda = 856 \text{ nm}$ for films in the fully oxidized and fully reduced forms.

Long term materials redox stability was evaluated via the chronoamperometric response to extended electrochemical switching, in the form of 10 000 cycles each comprising alternating potential impulses (50 s each) between 0.0 and 0.6 V. Based on the established correspondence between peak current and optical change for pure poly[Ni(3-Mesalen)] films,³³ the composite material response time was determined from the chronoamperometric response.⁴² A variation of peak current magnitude of 85% was used as the reference point. Before and after the chronoamperometric endurance tests, the modified electrodes were voltammetrically cycled.

2.5 Fabrication and characterization of a solid-state electrochromic device

The ECD based on GFNPs@poly[Ni(3-Mesalen)] polymer film was fabricated using a photopolymerizable electrolyte produced from HEMA monomer, containing: 6.0 g of a 0.1 mol. dm⁻³ LiClO₄ solution in EC:PC (1:1), 6.0 mg of BME photoinitiator, 1.5 g of HEMA photoreactive monomer and 60 mg of NPG reticulant agent. The electrodeposition of the electrochromic nanocomposite was performed in a two electrode cell with ITO/PET substrates (4.5 cm × 4.5 cm), in which one acts as the working electrode and the other as the counter electrode of the device. A frame (spacer) of double adhesive tape was bound between the two electrodes and the photopolymerizable electrolyte (0.7 cm³) was slowly injected in the remaining space between them. The device was then placed in a UV curing system (UV Omnicure S2000) equipped with a Hg lamp, for 30 minutes to promote the electrolyte photopolymerization.

The redox processes of the assembled ECD were characterized by cycling the applied potential in the range -1.2 to 1.4 V, for 10 scans, at $\nu = 0.01 \text{ V s}^{-1}$. The electrochromic performance was evaluated by chronoamperometry (see above) over the course of 10 000 redox cycles (between -0.75 V and 0.60 V; 60 s hold at each value). Note that, in this two electrode configuration (with no reference electrode) the potentials are necessarily slightly different to the three electrode cell configuration.

3. RESULTS AND DISCUSSION

3.1 Electrochemical preparation and characterization of the nanocomposite

The cyclic voltammograms obtained during the electropolymerization of the nanocomposite are depicted in Figure 1 (for comparison, cyclic voltammograms obtained during the electropolymerization of the pure polymer film are shown in Figure S4).

Qualitatively, the two voltammetric responses are very similar, which suggests that the presence of GFNPs did not substantively change the electropolymerization mechanism of poly[Ni(3-Mesalen)].

Figure 1. Cyclic voltammetric responses during the composite film electrodeposition onto ITO/PET. The deposition medium was a suspension of 0.5% (w/w) GFNPs in 1.0 mmol dm⁻³ [Ni(3-Mesalen)] dissolved in LiClO₄ (0.1 mol. dm⁻³)/CH₃CN. Voltammetric conditions: 30 scans, between -0.2 and 1.3 V (vs Ag/AgCl, 1 mol. dm⁻³); $\nu = 0.1 \text{ V s}^{-1}$.

The two anodic peaks (at 0.91 V and 1.07 V) observed in the first anodic deposition half-cycle correspond to Ni(II) monomer oxidation and subsequent formation of oligomers near the electrode surface. During the cathodic scan the two peaks (at 0.69 V and 0.19 V) are attributed to reduction of the resulting nanocomposite film. In the second cycle a new anodic peak is generated at 0.35 V, which corresponds to the oxidation of the as-prepared nanocomposite deposited in the previous scan. The magnitudes of the redox peaks increased continuously with potential cycling, indicating progressive film

deposition onto the ITO/PET. Visually, this was confirmed by the observation of a greenish, translucent film on the ITO/PET surface.

The voltammetric responses for the 5th scans, of the as-prepared nanocomposite film and a pure polymer film (for comparison), are depicted in Figure 2. The individual cyclic voltammograms for film conditioning are shown in Figure S5 and the peak potential values for the 1st and 5th scans are presented in Table S1.

Figure 2. Cyclic voltammograms acquired during redox switching of pure poly[Ni(3-Mesalen)] (black line) and GFNPs@poly[Ni(3-Mesalen)] nanocomposite (orange line) films. Solution: (a) LiClO₄ (0.1 M)/CH₃CN; (b) LiClO₄ (0.1 M)/PC. Scan rate, $\nu = 0.01 \text{ V s}^{-1}$. Films prepared with 30 electropolymerization cycles; electroactive coverages (a) $\Gamma \approx 180$ and (b) $\Gamma \approx 195 \text{ nmol cm}^{-2}$.

The cyclic voltammograms of GFNPs@poly[Ni(3-Mesalen)] in LiClO₄/CH₃CN (Figure S5 B) show a primary electrochemical process at $E_{\text{pa}} \approx 0.31 \text{ V}$ and two less significant processes at $E_{\text{pa}} \approx 0.78 \text{ V}$ and at $E_{\text{pa}} \approx 1.02 \text{ V}$ (for the 5th scan), in the anodic half cycle. In the reverse sweep, two electrochemical processes are identified, one at $E_{\text{pc}} \approx 0.23 \text{ V}$ and another with higher current intensity at $E_{\text{pc}} \approx 0.67 \text{ V}$. In 0.1 mol dm^{-3}

LiClO₄/PC solution the voltammetric response (Figure S5 D) is qualitatively very similar, although both peaks moved positively. In general, the pattern of *i*-*E* responses for the nanocomposite is essentially the same as for the pure polymer itself; the overlay of the two responses in Figure 2 makes the point clearly. It is also worth mentioning that both films show slight shifts of the peak potentials from the 1st scan to the 5th scan (Table S1 and Figure S5); this is attributed to the “film conditioning” behavior observed for poly[Ni(*salen*)]^{33,43} and indeed typical of many other electroactive films.

During redox switching of the nanocomposite film its electrochromic behavior was readily visible by eye, analogous to the behavior of poly[Ni(3-Mesalen)].³³ The first ($E_{pa} \approx 0.31$ V) and the second ($E_{pa} \approx 0.78$ V) anodic peaks correspond to yellow/green and green/reddish color changes, respectively. The first ($E_{pc} \approx 0.67$ V) and the second ($E_{pc} \approx 0.23$ V) cathodic peaks are associated with the inverse color changes. When redox switching is performed in PC the color change to red is not very pronounced; this is quantified by spectroelectrochemical measurements presented below (see section 3.3).

Figure 3. Plot of the surface coverage, Γ , with the number of polymerization scans employed for poly[Ni(3-Mesalen)] (■) and GFNPs@poly[Ni(3-Mesalen)] nanocomposite (●) films.

Figure 3 shows the dependence of the electroactive surface coverage on the number of polymerization scans for both films. The (apparent) electroactive surface coverage of pure poly[Ni(3-Mesalen)] only increases linearly up to 30 scans of polymerization; it then reaches a plateau at $\Gamma \approx 180 \text{ nmol cm}^{-2}$. This limitation is most probably a consequence of charge transport limitations. For the graphene-based nanocomposite the electroactive surface coverage continues to increase beyond this value. After 30 polymerization cycles, the electroactive surface coverage is $\Gamma \approx 195 \text{ nmol cm}^{-2}$ and after 60 cycles it reaches $\Gamma \approx 325 \text{ nmol cm}^{-2}$. This behavior is indicative of the successful incorporation of GFNPs into the [Ni(3-Mesalen)] polymeric matrix, which it is expected to increase the internal surface area and free volume, and thereby enhance ion intercalation through the polymeric matrix. The rigid nature of the GFNPs also prevents collapse of the film, so this increased porosity is maintained.

3.2 Compositional and morphological characterization

SEM micrographs (secondary electron (SE) and backscattered electron (BSE) modes) of the nanocomposite and pure poly[Ni(3-Mesalen)] deposited on ITO/PET are shown in Figure 4 and Figures S6 and S7, respectively. The nanocomposite morphology is similar to that of the pure polymer film. The surface is heterogeneous, with a mixture of thicker granular regions and smoother thinner regions. In Figure 4A, graphene clusters are easily observable (see orange marked region), confirming GFNP incorporation. Images acquired at higher magnification (Figure 4A') show disordered clusters of graphene nanoplatelets wrapped in a thin layer of polymeric. While the images do not

provide direct evidence of bonding, it is reasonable to speculate on the presence of π - π or hydrophobic interactions between the polymer and graphene nanoplatelets.

Figure 4. SEM micrographs of GFNPs@poly[Ni(3-Mesalen)] nanocomposite in SE mode. Scale bars indicate size. Panel A' is a magnification of the region marked in orange in panel A: graphene platelets are clearly visible.

SEM micrograph analysis was accomplished using BSE imaging mode and EDS spectra (Figure S7). Data for the GFNPs@poly[Ni(3-Mesalen)] nanocomposite show that the rougher regions (marked Z1 and Z2 in Figure S7) correspond to thicker film clusters;

this is deduced from the higher Ni content (from the polymeric film) in these regions. The polymer obscures the underlying ITO/PET substrate, so the In signal here is attenuated. Conversely, in the smoother (thinner) regions (marked Z3 in Figure S7), the Ni signal is smaller and the lesser coverage of polymer results in less attenuation of the In signal. A similar distribution of these elements was found for pure polymer films (Figure S6).

XPS was used to obtain surface compositional information for nanocomposite films (emersed in the reduced state) for comparison with that obtained for pure poly[Ni(3-Mesalen)] films. To explore any possible redox driven structural modifications, both films were subjected to 10 000 electrochemical cycles (potential pulses between $E = 0.0$ V and 0.6 V; 50 s hold at each value) and, after emersion in the reduced state, characterized by XPS. Table 1 summarizes the surface atom compositions.

Table 1. Atom ratios of relevant elements for pristine poly[Ni(3-Mesalen)] and GFNPs@poly[Ni(3-Mesalen)] films, as-prepared and after 10 000 electrochemical cycles (each comprising 50 s impulses to $E = 0.0$ V and 0.6 V).

Electrochromic Material	Atom%						Atom Ratio		
	Ni	C	N	O	Cl	Li	N/Ni	O/Ni	Cl/Ni
poly[Ni(3-Mesalen)]									
As-prepared	1.5	83.1	3.9	11.3	0.1	ND	2.6	7.5	0.1
After 10 000 cycles	1.5	54.6	5.5	27.3	5.1	5.1	3.7	18.2	3.4
GFNPs@poly[Ni(3-Mesalen)]									
As-prepared	1.6	82.9	4.4	11.0	0.1	ND	2.8	6.9	0.1
After 10 000 cycles	1.4	48.6	5.2	29.1	6.7	9.0	3.7	20.8	4.8

For both films, the XPS results unsurprisingly show the presence of the constituent elements of the polymeric film and graphene nanoplatelets. However, they also permit observation of the presence of entrapped supporting electrolyte, via the Li and Cl responses. Considering the composition of polymer and graphene nanoplatelets, Cls and

O1s XPS signals from the GFNPs@poly[Ni(3-Mesalen)] nanocomposite have contributions from both GFNPs and poly[Ni(3-Mesalen)]; thus, their qualitative presence does not lead to unambiguous conclusions. However, quantitative considerations of the atom ratios can provide valuable information.

The analysis of XPS-derived surface atom ratios before and after electrochemical cycling reveals variations for both pure and nanocomposite films. The main differences are the substantial increase of O/Ni and Cl/Ni atomic ratios and the detection of a considerable amount of Li in both materials (5.1% and 9.0% for poly[Ni(3-Mesalen)] and the nanocomposite, respectively) following the chronoamperometric test. These results are attributed to the uptake of the electrolyte components, responsible for charge neutralization during the film redox process. The O/Cl atom ratios are 5.4 and 4.3 for the pure polymer and the nanocomposite, respectively, in reasonable agreement with perchlorate stoichiometry and consistent with previous reports.^{43,44}

Surface atom ratios before and after electrochemical activity clearly reveal the occurrence of greater uptake of the supporting electrolyte by GFNPs@poly[Ni(3-Mesalen)]. Specifically, for the pure polymer, the O/Ni and Cl/Ni ratios increase, respectively, by factors of 2.4 and 34 after 10 000 redox cycles, whereas for the nanocomposite film the corresponding atom ratios increase by factors of 3.0 and 48. Moreover, after 10 000 redox cycles the Li/Ni ratio increase is 3.4 times for the pure polymer and 6.4 for the nanocomposite. The increases in atom ratios, which are a measure of the electrolyte:polymer ratio, support the notion of increased free volume and consequent enhancement of ion intercalation into the polymer matrix in the presence of GFNPs.

3.3 Spectroelectrochemical characterization

Absolute UV-Vis spectra acquired during the oxidation of pure polymer and GFNPs@poly[Ni(3-Mesalen)] nanocomposite films in 0.1 mol dm⁻³ LiClO₄/PC are depicted in Figure 5. The UV-Vis spectra obtained during film reduction were omitted for simplicity. Qualitatively similar to the pure poly[M(*salen*)] film,³³ four characteristic electronic bands, dependent on potential and with identical profiles, are identified at $\lambda = 335$ nm, $\lambda = 401$ nm, $\lambda = 517$ nm and $\lambda = 857$ nm for GFNPs@poly[Ni(3-Mesalen)]. Quantitatively, two significant differences are highlighted in the nanocomposite spectra as compared to the pure polymer film spectra: the absorbance of the band at $\lambda = 517$ nm is clearly diminished (to the point of being almost undetectable) and the intensity increase of the band at $\lambda = 857$ nm is slightly more pronounced than for the corresponding poly[Ni(3-Mesalen)] film band.

Figure 5. UV-visible spectra of (a) poly[Ni(3-Mesalen)] ($\Gamma = 180$ nmol cm⁻²) and (b) GFNPs@poly[Ni(3-Mesalen)] ($\Gamma = 195$ nmol cm⁻²) films. Data were acquired during redox switching in background electrolyte (LiClO₄ (0.1 mol. dm⁻³)/PC), during the anodic half cycle of

a voltammetric scan (from -0.2 to 1.3 V at $\nu = 0.02 \text{ V s}^{-1}$). The first spectrum acquired is marked in orange (→) and the last one in green (←); arrows indicate scan direction.

The band profiles and their dependence on potential (notably the peak absorbance vs. potential profiles) are presented in Figure S8. These profiles reveal similarities and differences, which are more readily appreciated via the differential spectra shown in Figures S9 and S10 for the pure poly[Ni(3-Mesalen)] film and the GFNPs@poly[Ni(3-Mesalen)] nanocomposite, respectively. Analysis reveals three distinct patterns of behavior for the nanocomposite and pure polymer films. First, the bands (for both materials) at $\lambda = 333\text{-}335 \text{ nm}$ *decrease* monotonically in intensity with increasing potential. Second, the bands at $\lambda = 398\text{-}401 \text{ nm}$ and $\lambda = 857 \text{ nm}$, show a continuous *increase* in intensity with potential, both commencing at $E \approx 0.3 \text{ V}$ then plateauing at $E \approx 0.6 \text{ V}$ and at $E \approx 0.8 \text{ V}$, respectively. Third, the bands at $\lambda = 514\text{-}517 \text{ nm}$ also increase in intensity with potential, but the onset of this increase is delayed in terms of potential ($E \approx 0.9 \text{ V}$).

The *Abs* vs. *Q* profiles for the graphene-based nanocomposite are shown in Figure S11, with the corresponding profiles for the pure poly[Ni(3-Mesalen)] film in Figure S12. The absence of hysteresis in *Abs* vs. *Q* plots of the nanocomposite (Figure S11) contrasts with the behavior for pure poly[Ni(3-Mesalen)] (Figure S12) and suggests that the presence of GFNPs promotes charge transport within the poly[Ni(3-Mesalen)] network. Molar extinction coefficients, ϵ , at λ_{max} for each electronic band were determined from the slopes of *Abs* vs. *Q* profiles, where absorbance changes are maximal, using Equation 1⁴⁵. The calculated values and the energies of the transitions are summarized in Table 2.

Table 2. Electronic bands and respective molar extinction coefficients for pristine poly[Ni(3-Mesalen)] and GFNPs@poly[Ni(3-Mesalen)] films.

Electrochromic Material	λ/nm	$10^{-3} \epsilon / \text{cm}^{-1} \text{mol}^{-1} \text{dm}^3$	Energy/ eV	$\epsilon_{\text{nanocomposite}} / \epsilon_{\text{poly[Ni(salen)]}}$
poly[Ni(3-Mesalen)]	333	3.32	3.72	
	398	1.67	3.11	
	514	3.71	2.41	
	857	5.62	1.45	
GFNPs@poly[Ni(3-Mesalen)]	335	2.66	3.70	0.80
	401	1.62	3.09	0.97
	517	2.79	2.40	0.75
	857	5.82	1.45	1.03

The order of magnitude of the molar extinction coefficients is consistent with previously reported values for pure poly[M(*salen*)] films.^{33,44} The energies of the transitions and the ϵ values indicate that the bands correspond to electronic transitions between states with substantial contribution from the ligand orbitals. The interpretation of these spectroscopic data for the nanocomposite can be made according to the polaronic model, as recently done for poly[Ni(3-Mesalen)]: i) the band at $\lambda = 335$ nm ($E_g = 3.70$ eV) is attributed to the intervalence transition; ii) the bands at $\lambda = 401$ nm ($E_g = 3.09$ eV) and $\lambda = 857$ nm ($E_g = 1.45$ eV) are assigned to transitions inside the band gap; iii) the band at $\lambda = 517$ nm ($E_g = 2.40$ eV) is ascribed to charge transfer transitions between the metal center and the oxidized ligand.

The energies of the electronic bands of the graphene-based nanocomposite are similar to those of the pure polymer film, revealing that the electronic structure of the metallopolymer is essentially unperturbed by incorporation of GFNPs. Nonetheless, there were considerable variations amongst the ϵ values of the nanocomposite electronic bands.

While the ratio $\varepsilon_{\text{nanocomposite}}/\varepsilon_{\text{poly[Ni(3-Mesalen)]}}$ for the bands at $\lambda = 398\text{-}401$ nm and $\lambda = 857$ nm is very close to 1 (0.97 and 1.03, respectively), the ε values of the bands $\lambda = 333\text{-}335$ nm and $\lambda = 514\text{-}517$ nm decrease by 20% and 25%, respectively, when GFNPs are entrapped in the poly[Ni(3-Mesalen)] film. In the specific case of the charge transfer band ($\lambda = 514\text{-}517$ nm), the decrease of the ε values may indicate an enhancement of the nanocomposite stability towards overoxidation. This practical value of this outcome, which is intrinsically associated with the reddish coloration state, is exploited below.

3.4 Electrochromic properties

Detailed evaluation of the electrochromic properties was performed for the yellow $\leftrightarrow$ green transition. Experimentally, polymer and composite films prepared using 30 electropolymerization cycles were compared. These have similar electroactive surface coverages: $\Gamma \approx 195$ nmol cm⁻² for GFNPs@poly[Ni(3-Mesalen)] and $\Gamma \approx 180$ nmol cm⁻² for poly[Ni(3-Mesalen)]. To optimize the electrochromic performance of poly[Ni(3-Mesalen)] film, LiClO₄/PC was used as the supporting electrolyte.

Figure 6 presents the optical density change, ΔOD , across a wide range of wavelengths for representative GFNPs@poly[Ni(3-Mesalen)] and pure poly[Ni(3-Mesalen)]. For both materials, high values of ΔOD are achieved in the range $\lambda \approx 615\text{-}1100$ nm: the maximum ΔOD is noticeably higher for the nanocomposite ($\Delta OD = 1.43$, $\lambda = 856$ nm) than for the pure polymer ($\Delta OD = 1.15$, $\lambda = 856$ nm). Another interesting feature is observed in the range $\lambda \approx 444\text{-}570$ nm: there is an inversion of behavior in that the change in optical density for the pure polymer film is superior ($\Delta OD_{\text{max}} = 0.52$), to that for the nanocomposite ($\Delta OD_{\text{max}} = 0.33$). This observation is in agreement with the behavior of electronic bands previously reported, namely the decrease of the electronic band intensity at $\lambda = 517$ nm upon the incorporation of GFNPs in the polymeric structure.

The ΔT values (estimated at $\lambda = 856$ nm) were 58.8% for poly[Ni(3-Mesalen)] and 53.2% for GFNPs@poly[Ni(3-Mesalen)] nanocomposite films.

Figure 6. Optical density, ΔOD , of pure poly[Ni(3-Mesalen)] ($I=180$ nmol cm⁻²) (black line) and GFNPs@poly[Ni(3-Mesalen)] ($I=195$ nmol cm⁻²) (orange line), at various wavelengths.

The electrochemical stability of both electrochromic materials was evaluated by chronoamperometry (Figure 7). After 10 000 electrochemical cycles the loss of charge was 7% for the GFNPs-based nanocomposite and 8% for the pure poly[Ni(3-Mesalen)] film, indicating that graphene incorporation contributed to electrochemical stability. An additional stability test was performed for a composite prepared from a [Ni(3-Mesalen)] monomer solution containing 1.5 wt.% (GFNPs/[Ni(3-Mesalen)] wt.%) of graphene nanoplatelets. The charge loss of 11% for 4600 electrochemical cycles (5 days of activity) (Figures S13 and S14) indicates that increased GFNP content is not advantageous.

Figure 7. Upper panel: extended timescale chronoamperograms of poly[Ni(3-Mesalen)] film (red) and GFNPs@poly[Ni(3-Mesalen)] nanocomposite (orange), acquired in LiClO_4 (0.1 mol. dm^{-3})/PC, by applying 2 potential impulses of 50 seconds each one per electrochemical cycle, with potential alternation between 0.0 and 0.6 V. Lower panel: magnification of the first 3 electrochemical cycles, showing time responses and respective photographs of the materials in the different oxidation states.

Voltammetric responses acquired before and after the chronoamperometric study, for both materials, are shown in Figure S15. Qualitatively, a slight displacement of peak position and a current intensity decrease are observed for both materials, more so for the poly[Ni(3-Mesalen)] film. In terms of charge variation, the loss is about 16.6% for the

pure polymeric film and practically zero (ca. 0.2%) for the graphene-based nanocomposite. These observations indicate that GFNP inclusion promotes longevity of poly[Ni(3-Mesalen)] electrochemical properties.

The inset in Figure 7 shows the current-time response for 3 electrochemical cycles for pure polymer and nanocomposite films. The values reveal the existence of some asymmetry in the times required for green and yellow coloration. This has been reported for other electrochromic polymers and is attributed to several factors such as switching direction, polymer conductivity, electric field strength and ion transport rate variations during film solvation.⁸ The inclusion of GFNPs in the poly[Ni(3-Mesalen)] structure significantly accelerates switching: the response time for green coloration is decreased by 50% (from 49 to 24 s) and for yellow coloration by 60% (from 31 to 12 s). The incorporation of GFNPs provides alternative conductive pathways and contributes to enhanced porosity, a key factor in the transport of charge compensating ions during polymer redox switching.

To evaluate the influence of prolonged electrochemical activity on response time, the same study was performed after four different intervals of chronoamperometric observations (50 s and 1.35, 5 and 12 days); the results are summarized in Table S2. The main difference is related to the switching time for yellow coloration in the case of the single polymer component, which increased 29% after 10 000 electrochemical cycles. The beneficial effect of GFNPs in stability terms is underscored by the fact that the corresponding increase of switching time for the composite film was only ca. 7%.

Based on the above findings – improved electrochemical and electrochromic properties for the GFNPs@poly[Ni(3-Mesalen)] nanocomposite film and optimal conditions – we now describe the assembly of a flexible solid-state ECD.

3.5 Fabrication and characterization of an electrochromic device

The schematic representation of the fabricated ECD are presented in Figure 8; its electrochemical and electrochromic behavior were characterized by cyclic voltammetry and chronoamperometry. Note that, unlike the electrochemical studies previously described, the potential values presented in this section correspond to potential differences between the working and the counter electrodes since the practical two-electrode device does not include a reference electrode.

The cyclic voltammogram of the ECD is shown in Figure S16. The observed peaks are broad and the anodic and cathodic processes occur at $E = 0.88$ V and at $E = -0.03$ V/-0.75 V, respectively. The voltammograms exhibited a reproducible and reversible profile after being cycled five times, consistent with the established electrochemical stability of the component materials.

It was possible to follow the device color change by eye during the redox process. When the potential was alternated between $E = -0.75$ V and $E = 0.6$ V the color changed uniformly between green and yellow (Figure 8). The images show that the device simultaneously presents the two colors because when the electrochromic nanocomposite deposited in one of the ITO/PET substrates is being oxidized (therefore presenting the green color), the electrochromic nanocomposite deposited in the other substrate is being reduced (yellow color). This is possible due to the transparency of the electrolyte that enables the simultaneous visualization of two distinct images with different colors at the same face of the device.

Figure 8. Upper panel: schematic representation of the ECD structure. Lower panels: pictures of the ECD in different oxidation states, showing the visible color contrast between electrochromic materials deposited on the two ITO/PET substrates (working and counter electrodes).

Figure S17 shows the chronoamperograms obtained after 15 days of continuous ECD redox switching. The ECD showed outstanding long-term stability, which is crucial for electrochromic applications: during 15 days of uninterrupted electrochemical activity, the loss of charge was about 3% and the device maintained electrochromic performance. The comparison between the cyclic voltammograms acquired before and after the chronoamperometric study (Figure S18) also reveals that the redox processes do not show significant qualitative change, although the global charge is decreased by 15%. The time response (taken at 50% variation of peak current magnitude) during continuous electrochemical switching was determined at four points (see Table 3). The results show

that the response time stabilizes after a slight decrease in the beginning of the chronoamperometry. The higher response time in the initial few cycles may be attributable to resistive effects in the polymer film.¹¹

Table 3. Comparison between the response time for green coloration (t_1) and yellow coloration (t_2) of the ECD during extended redox switching test.

Sampling point/days	Response time/s		% of variation ¹
1.0	t_1	23.9	
	t_2	12.0	
5.1	t_1	23.0	-3.9
	t_2	11.5	-4.1
10.0	t_1	23.1	-3.6
	t_2	12.1	0.8
15.0	t_1	23.0	-3.7
	t_2	11.5	-4.1

¹ Percentage variation determined with respect to response time after 1 day of electrochemical activity.

4. CONCLUSIONS

A novel electrochromic system involving a composite material based on poly[Ni(3-Mesalen)] and graphene nanoplatelets was successfully fabricated, characterized (electrochemically, optically, compositionally and morphologically) and implemented in a prototype electrochromic device.

The simplistic hypothesis that a composite material might display the positive attributes of both components was more than realised: synergistic effects were also observed. The inclusion of GFNPs in poly[Ni(3-Mesalen)] films did not substantively change the redox or optical properties of the polymer, but did result in their dynamics (switching rate) and longevity (stability to extended switching operations) being substantially enhanced. GFNP incorporation was established by direct observation (SEM)

and the disordered clustering of the nanoparticles resulted in increased free volume that was (at least in part) taken up by electrolyte (as determined by XPS).

Electrochemical characterization showed retention of similar electrochemical responses for GFNPs@poly[Ni(3-Mesalen)] nanocomposite films as compared to the pure polymer films: the irreversible electropolymerization and reversible polymer redox processes are retained in the presence of graphene nanoplatelets. The *direct* result of composite formation was increased electronic conductivity (from the GFNPs) and the *indirect* result was increased ionic conductivity (from incorporated electrolyte). Together these improved and extended film redox state switching rate; in particular the response times for both green and yellow coloration were roughly halved.

Based on these advances, a solid-state ECD based on the graphene-[Ni(3-Mesalen)] nanocomposite was successfully fabricated using a flexible ITO/PET substrate. The electrochemical evaluation revealed excellent longevity during an extended (15 day) switching test; this performance is substantially superior to the previously reported electrochromic device based on a poly[Ni(3-Mesalen)] film.³³ Overall, this work signals the potential of graphene-Ni-*salen* polymer nanocomposites as valuable materials for EC applications, such as optical/electronic displays and paper-like applications.

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Supporting Information. Profile of the graphene platelets concentration with the sonication time, SEM and TEM micrographs and XPS spectra of graphite powder and graphene nanoplatelets, cyclic voltammograms of the poly[Ni(3-Mesalen)] electrodeposition, complete voltammetric responses, SEM micrographs, EDS spectra, UV-Vis spectra and plots of absorbance vs. E and differential absorbance vs. Q of poly[Ni(3-Mesalen)] and GFNPs@poly[Ni(3-Mesalen)] films, cyclic voltammogram and chronoamperogram of the nanocomposite prepared with 1.5% wt. of GFNPs and of the assembled electrochromic device, peak potentials of the cyclic voltammograms obtained during redox switching and response times along the chronoamperometric study.

REFERENCES

- (1) Mortimer, R. J. Electrochromic Materials. *Annu. Rev. Mater. Res.* **2011**, *41* (1), 241–268.
- (2) Rosseinsky, D. R.; Mortimer, R. J. Electrochromic Systems and the Prospects for Devices. *Adv. Mater.* **2001**, *13*, 783–793.
- (3) Beaupré, S.; Dumas, J.; Leclerc, M. Toward the Development of New Textile / Plastic Electrochromic Cells Using Triphenylamine-Based Copolymers. *Chem. Mater.* **2006**, *18*, 4011–4018.
- (4) Tavanai, H.; Kaynak, A. Effect of Weight Reduction Pre-Treatment on the Electrical and Thermal Properties of Polypyrrole Coated Woven Polyester Fabrics. *Synth. Met.* **2007**, *157* (18–20), 764–769.
- (5) Yang, D.-J.; Hsu, C.-Y.; Lin, C.-L.; Chen, P.-Y.; Hu, C.-W.; Vittal, R.; Ho, K.-C. Fast Switching Prussian Blue Film by Modification with Cetyltrimethylammonium Bromide. *Sol. Energy Mater. Sol. Cells* **2012**, *99*, 129–134.
- (6) Su, T.-H.; Hsiao, S.-H.; Liou, G.-S. Novel Family of Triphenylamine-Containing, Hole-Transporting, Amorphous, Aromatic Polyamides with Stable Electrochromic Properties. *J. Polym. Sci. Part A Polym. Chem.* **2005**, *43* (10), 2085–2098.
- (7) Gunbas, G.; Toppare, L. Electrochromic Conjugated Polyheterocycles and Derivatives-- Highlights from the Last Decade towards Realization of Long Lived Aspirations. *Chem.*

Commun. **2012**, *48* (8), 1083–1101.

- (8) Amb, C. M.; Dyer, A. L.; Reynolds, J. R. Navigating the Color Palette of Solution-Processable Electrochromic Polymers †. *Chem. Mater.* **2011**, *23* (3), 397–415.
- (9) Mecerreyes, D.; Marcilla, R.; Ochoteco, E.; Grande, H.; Pomposo, J. A.; Vergaz, R.; Sánchez Pena, J. M. A Simplified All-Polymer Flexible Electrochromic Device. *Electrochim. Acta* **2004**, *49* (21), 3555–3559.
- (10) Deb, S. K. Opportunities and Challenges in Science and Technology of WO₃ for Electrochromic and Related Applications. *Sol. Energy Mater. Sol. Cells* **2008**, *92* (2), 245–258.
- (11) Wu, C.-G.; Lu, M.-I.; Chang, S.-J.; Wei, C.-S. A Solution-Processable High-Coloration-Efficiency Low-Switching-Voltage Electrochromic Polymer Based on Polycyclopentadithiophene. *Adv. Funct. Mater.* **2007**, *17* (7), 1063–1070.
- (12) Granqvist, C. G.; Lansåker, P. C.; Mlyuka, N. R.; Niklasson, G. A.; Avendaño, E. Progress in Chromogenics: New Results for Electrochromic and Thermochromic Materials and Devices. *Sol. Energy Mater. Sol. Cells* **2009**, *93* (12), 2032–2039.
- (13) Kraft, A.; Rottmann, M. Properties, Performance and Current Status of the Laminated Electrochromic Glass of Gesimat. *Sol. Energy Mater. Sol. Cells* **2009**, *93* (12), 2088–2092.
- (14) Beaujuge, P. M.; Reynolds, J. R. Color Control in Pi-Conjugated Organic Polymers for Use in Electrochromic Devices. *Chem. Rev.* **2010**, *110* (1), 268–320.
- (15) Hou, J.; Shao, Y.; Ellis, M. W.; Moore, R. B.; Yi, B. Graphene-Based Electrochemical Energy Conversion and Storage: Fuel Cells, Supercapacitors and Lithium Ion Batteries. *Phys. Chem. Chem. Phys.* **2011**, *13* (34), 15384–15402.
- (16) Pumera, M. Graphene-Based Nanomaterials and Their Electrochemistry. *Chem. Soc. Rev.* **2010**, *39* (11), 4146–4157.
- (17) Stankovich, S.; Dikin, D. a; Dommett, G. H. B.; Kohlhaas, K. M.; Zimney, E. J.; Stach, E. A.; Piner, R. D.; Nguyen, S. T.; Ruoff, R. S. Graphene-Based Composite Materials. *Nature* **2006**, *442* (7100), 282–286.
- (18) Geim, A. K.; Novoselov, K. S. The Rise of Graphene. *Nat. Mater.* **2007**, *6* (3), 183–191.
- (19) Guldi, D. M.; Sgobba, V. Carbon Nanostructures for Solar Energy Conversion Schemes. *Chem. Commun.* **2011**, *47* (2), 606–610.

- (20) Avouris, P. Graphene: Electronic and Photonic Properties and Devices. *Nano Lett.* **2010**, *10*, 4285–4294.
- (21) Bonaccorso, F.; Sun, Z.; Hasan, T.; Ferrari, A. C. Graphene Photonics and Optoelectronics. *Nat. Photonics* **2010**, *4* (9), 611–622.
- (22) Guo, S.; Dong, S. Graphene Nanosheet: Synthesis, Molecular Engineering, Thin Film, Hybrids, and Energy and Analytical Applications. *Chem. Soc. Rev.* **2011**, *40* (5), 2644–2672.
- (23) Kuilla, T.; Bhadra, S.; Yao, D.; Kim, N. H.; Bose, S.; Lee, J. H. Recent Advances in Graphene Based Polymer Composites. *Prog. Polym. Sci.* **2010**, *35* (11), 1350–1375.
- (24) Sun, Y.; Shi, G. Graphene/polymer Composites for Energy Applications. *J. Polym. Sci. Part B Polym. Phys.* **2013**, *51* (4), 231–253.
- (25) Basnayaka, P. A.; Ram, M. K.; Stefanakos, L.; Kumar, A. High Performance Graphene-Poly (O-Anisidine) Nanocomposite for Supercapacitor Applications. *Mater. Chem. Phys.* **2013**, *141* (1), 263–271.
- (26) Österholm, A.; Lindfors, T.; Kauppila, J.; Damlin, P.; Kvarnström, C. Electrochemical Incorporation of Graphene Oxide into Conducting Polymer Films. *Electrochim. Acta* **2012**, *83*, 463–470.
- (27) Lim, Y. S.; Tan, Y. P.; Lim, H. N.; Tan, W. T.; Mahnaz, M. A.; Talib, Z. A.; Huang, N. M.; Kassim, A.; Yarmo, M. A. Polypyrrole/graphene Composite Films Synthesized via Potentiostatic Deposition. *J. Appl. Polym. Sci.* **2013**, *128* (1), 224–229.
- (28) Basavaraja, C.; Noh, G. T.; Huh, D. S. Chemically Modified Polyaniline Nanocomposites by poly(2-Acrylamido-2-Methyl-1-Propanesulfonicacid)/graphene Nanoplatelet. *Colloid Polym. Sci.* **2013**, *291*, 2755–2764.
- (29) Reddy, B. N.; Deepa, M.; Joshi, A. G.; Srivastava, A. K. Poly(3,4-Ethylenedioxythiophene) Wrapped by Reduced Graphene Oxide: How Conduction Behavior at Nanolevel Leads to Increased Electrochemical Activity. *J. Phys. Chem. C* **2011**, *115* (37), 18354–18365.
- (30) Sheng, K.; Bai, H.; Sun, Y.; Li, C.; Shi, G. Layer-by-Layer Assembly of Graphene/polyaniline Multilayer Films and Their Application for Electrochromic Devices. *Polymer (Guildf)*. **2011**, *52* (24), 5567–5572.
- (31) Ma, L.; Zhao, P.; Wu, W.; Niu, H.; Cai, J.; Lian, Y.; Bai, X.; Wang, W. RGO Functionalised with Polyschiff Base: Multi-Chemical Sensor for TNT with Acidochromic

- and Electrochromic Properties. *Polym. Chem.* **2013**, 4 (17), 4746.
- (32) Xiong, S.; Li, Z.; Gong, M.; Wang, X.; Fu, J.; Shi, Y.; Wu, B.; Chu, J. Covalently Bonded Polyaniline and Para-Phenylenediamine Functionalized Graphene Oxide: How the Conductive Two-Dimensional Nanostructure Influences the Electrochromic Behaviors of Polyaniline. *Electrochim. Acta* **2014**, 138, 101–108.
 - (33) Nunes, M.; Araújo, M.; Fonseca, J.; Moura, C.; Hillman, R.; Freire, C. High-Performance Electrochromic Devices Based on poly[(Ni(salen)]-Type Polymer Films. *ACS Appl. Mater. Interfaces* **2016**, 8, 14231–14243.
 - (34) Holm, R. H.; Everett, G. W.; Chakravorty, A. Metal Complexes of Schiff Bases and Beta-Ketoamines. *Prog. Inorg. Chem.* **1966**, 7, 83.
 - (35) Khan, U.; Porwal, H.; O'Neill, A.; Nawaz, K.; May, P.; Coleman, J. N. Solvent-Exfoliated Graphene at Extremely High Concentration. *Langmuir* **2011**, 27 (15), 9077–9082.
 - (36) Hernandez, Y.; Nicolosi, V.; Lotya, M.; Blighe, F. M.; Sun, Z.; De, S.; McGovern, I. T.; Holland, B.; Byrne, M.; Gun'Ko, Y. K.; et al. High-Yield Production of Graphene by Liquid-Phase Exfoliation of Graphite. *Nat. Nanotechnol.* **2008**, 3 (9), 563–568.
 - (37) Khan, U.; O'Neill, A.; Lotya, M.; De, S.; Coleman, J. N. High-Concentration Solvent Exfoliation of Graphene. *Small* **2010**, 6 (7), 864–871.
 - (38) Quintana, M.; Spyrou, K.; Grzelczak, M.; Browne, W. R.; Rudolf, P.; Prato, M. Functionalization of Graphene. **2010**, 4 (6), 3527–3533.
 - (39) Dale, S. M.; Glidle, A.; Hillman, A. R. Spectroelectrochemical Observation of Poly(benzo[c]thiophene) N- and P-Doping. *J. Mater. Chem.* **1992**, 2 (1), 99.
 - (40) Schott, M.; Lorrmann, H.; Szczerba, W.; Beck, M.; Kurth, D. G. State-of-the-Art Electrochromic Materials Based on Metallo-Supramolecular Polymers. *Sol. Energy Mater. Sol. Cells* **2014**, 126, 68–73.
 - (41) Xue, B.; Peng, J.; Xin, Z.; Kong, Y.; Li, L.; Li, B. High-Contrast Electrochromic Multilayer Films of Molybdenum-Doped Hexagonal Tungsten Bronze (Mo_{0.05}-HTB). *J. Mater. Chem.* **2005**, 15 (45), 4793.
 - (42) Kadam, P. M.; Tarwal, N. L.; Mali, S. S.; Deshmukh, H. P.; Patil, P. S. Enhanced Electrochromic Performance of F-MWCNT-WO₃ Composite. *Electrochim. Acta* **2011**, 58, 556–561.

- (43) Tedim, J.; Carneiro, A.; Bessada, R.; Patrcio, S.; Magalhes, A. L.; Freire, C.; Gurman, S. J.; Hillman, A. R. Correlating Structure and Ion Recognition Properties of [Ni(salen)]-Based Polymer Films. *J. Electroanal. Chem.* **2007**, *610* (1), 46–56.
- (44) Fonseca, J.; Tedim, J.; Biernacki, K.; Magalhes, A. L.; Gurman, S. . J.; Freire, C.; Hillman, A. R. Structural and Electrochemical Characterisation of [Pd(salen)]-Type Conducting Polymer Films. *Electrochim. Acta* **2010**, *55* (26), 7726–7736.
- (45) Fonseca, J.; Martinez, J.; Cunha-Silva, L.; Magalhes, A. L.; Duarte, M. T.; Freire, C. Insights into Electronic and Structural Properties of Novel Pd(II) Salen-Type Complexes. *Inorganica Chim. Acta* **2010**, *363* (14), 4096–4107.