

Flexible viologen electrochromic devices with low operational voltage using reduced graphene oxide electrodes

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ABSTRACT

Reduced graphene oxide (RGO) films have been electrodeposited on indium tin oxide coated polyethylene terephthalate substrates (ITO-PET) from graphene oxide (GO) solutions and the resulting flexible transparent electrodes have been used in electrochromic devices of ethyl viologen (EtV^{2+}). The electrochromic performance of devices with bare ITO-PET electrodes and ITO-PET coated with RGO has been compared. Under continuous cycling tests up to large voltages, the RGO film was oxidized and dispersed in the electrochromic mixture. The resulting

devices, which contained GO/RGO in the electrochromic mixture, showed lower switching voltage between the colored and bleached states. This electrocatalytic activity of the solution-phase GO/RGO pair towards the electrochemical reaction of the electrochromic redox couple (the dication EtV^{2+} and the radical cation $\text{EtV}^{+\cdot}$) enabled devices with higher optical contrast than those free of GO at a same applied voltage.

1. Introduction

Electrochromism is defined as a reversible change in the transmittance of a material as the result of an electrochemical oxidation or reduction.¹ The electroactive species change their optical absorption bands due to the gain or loss of electrons. Commercial interest in electrochromism is mainly focused on smart windows, mirrors and displays. In the simplest electrochromic devices, the electrochromic active molecules are dissolved in a medium interposed, as a single thin film, between the conductive inner surfaces of two transparent substrates. Among electrochromic materials, 1,1'-disubstituted-4,4'-bipyridinium salts (viologens) are a well-known class of cathodic electrochromic compounds displaying different colors depending on their oxidation state and the nature of the substituents at the nitrogen atoms.² Thus, with simple alkyl groups the dication species are colorless while the radical cations are blue/violet. The neutral, di-reduced compounds, formed by one-electron reduction of the radical cations or by direct two-electron reduction of the dications, show a weak color intensity.

In electrochromic devices (ECD), transparent conducting oxides (TCOs) and in particular tin-doped indium oxide (ITO), are the most commonly used electrode materials. However, ITO suffers of several drawbacks: Indium is becoming a scarce and expensive resource and ITO

exhibits serious technical limitations (deposition techniques are expensive, ITO films are fragile, sensitive to corrosion and have a relatively high refraction index). For these reasons, alternative materials to TCOs are being investigated such as organic polymers and nanomaterials. Among the organic polymers, poly(3,4-ethylenedioxy-thiophene) doped with poly(styrene sulfonate), PEDOT:PSS, is the leader in transparent conducting polymers. Thin coatings of metals, such as gold, and films of single-walled carbon nanotubes have also emerged as an alternative to ITO, with comparable transparency in the visible region and higher transparency in the 2–5- μm infrared region. Absorptive/transmissive polymer-based ECD have been assembled using single-walled carbon nanotubes on glass as electrode substrates.³

In this regard, the high transparency, electrical conductivity and chemical stability of graphene makes it an ideal electrode material for ECD as well as for many other electronic and optoelectronic applications such as solar cells,⁴ touch screens,⁵ light-emitting diodes,⁶ and photodetectors.⁷ In the field of electrochromism, after the first report of a graphene-based liquid crystal ECD,⁸ there has been a number of studies on the effect of graphene or reduced graphene oxide in the electrochromic properties of a wide range of materials.⁷⁻¹⁸ These have comprised both organic and inorganic electrochromic materials such as polyaniline,^{9,10} poly(3,4-ethylene dioxythiophene),¹¹ poly(3,4-ethylenedioxy pyrrole),¹² polynorbornenes,¹³ polyimide,¹⁴ polyamide,¹⁵ Prussian blue,¹⁶ nickel oxide,¹⁷ tungsten oxide¹⁸ and vanadium pentoxide.¹⁹

Most of these studies focus in the preparation and evaluation of the electrochromic performance of novel graphene/electrochromic material composite films in a three-electrode cell configuration. Overall, it is claimed that the composite assemblies show good electrochromic features such as fast color-switching speed, good cyclic stability or high coloration efficiency. However, only in few cases the performance of the hybrid system is benchmarked against the

graphene-free counterpart. This is the case of Zhao et al.,⁹ who demonstrated that polyaniline (PANI) on graphene-coated quartz electrodes showed much larger optical contrast and shorter switching time than PANI/ITO electrodes after 300 cycles, revealing the high electrochemical stability of graphene electrodes. Better cycling performance and faster switching speeds were also noted for NiO/RGO hybrid electrochromic films, which were attributed to the electrochemical stability of RGO and higher porosity of the hybrid film that facilitates electrolyte access.¹⁷

On the other hand, examples of fully assembled electrochromic devices integrating electrodes with graphene/electrochromic composite systems are scarce. In this paper, we report for the first time the preparation and spectroelectrochemical characterization of flexible ECD based on ethyl viologen (EtV^{2+}) sandwiched between two ITO-PET electrodes coated with RGO films. For comparative purposes, identical devices without the RGO coating (only ITO-PET) were also fabricated and their electrochromic performance assessed. Partial dissolution of the RGO film into the solution phase during potential cycling facilitated the redox reaction of the electrochromic system, which allowed lower switching voltage between the colored and bleached states and consequently higher optical contrasts at a same applied voltage for the ECD fabricated with RGO electrodes.

2. Experimental

2.1. Materials

1,1'-Diethyl-4,4'-bipyridinium dibromide (99%) was purchased from Aldrich and used without further purification. Hydroquinone (99.5%) was obtained from Riedel-de-Haën and 1-butyl-3-methylimidazolium tetrafluoroborate (99%) was supplied by Solvionic. Extra pure

propylene carbonate was purchased from Scharlau and ITO-coated PET slides ($R = 60 \Omega/\text{sq}$) were provided by Sheldahl.

2.2. Preparation of RGO-coated ITO-PET electrodes

Graphene oxide was produced by chemical exfoliation of natural graphite (Bay Carbon Inc., SP-1) according to the modified Hummers method.²⁰ Briefly, graphite was oxidized to graphite oxide in a $\text{H}_2\text{SO}_4/\text{KMnO}_4/\text{H}_2\text{O}_2$ mixture and subsequently exfoliated to graphene oxide by tip ultrasonication (3 h, ice bath) in aqueous solution. Unexfoliated graphite oxide was separated by centrifugation (90 minutes, 4000 rpm) and the resulting stable aqueous graphene oxide (GO) dispersion was used to coat the ITO-PET electrodes. The GO aqueous solution (0.1 mg mL^{-1}) was placed between two ITO-PET substrates (5 cm x 5 cm) separated by 2 mm thick spacers with the two conducting surfaces facing each other. The potential difference between the two electrodes was gradually increased until a visible film of reduced graphene oxide was deposited at the cathode side. The RGO films on ITO-PET used in the ECD were deposited by applying a 3.5 V voltage for 5 minutes, which led to very homogeneous deposits of $\sim 80\%T$ at 550 nm.

2.3. Fabrication of the electrochromic device

The electrochromic mixture was prepared by mixing 1,1'-diethyl-4,4'-bipyridinium dibromide (0.01g, 9 mM), hydroquinone (0.003 g, 9 mM), 1-butyl-3-methylimidazolium tetrafluoroborate (BMIBF₄, 1.6 g, 2 M) and propylene carbonate (2 g) for 1 hour at room temperature. The ECD was prepared by joining two identical electrodes (either bare or RGO-coated ITO-PET) with an adhesive tape (200 μm thick) placed along the whole perimeter, allowing two small channels in opposite corners to fill the device by capillarity with the electrochromic mixture.

2.4. Instrumentation and measurements

UV/Vis absorption spectra were measured in transmission mode in a Jasco V-570 spectrophotometer. Transmittance of the ECD was registered using a film holder accessory for solid samples. All electrochemical measurements were carried out with a Biologic MPG potentiostat-galvanostat. Cyclic voltammetry of deaerated EtV^{2+} solutions with increasing concentration of GO was carried out in three-electrode configuration with Pt foils as working and counter electrode and Ag wire as pseudoreference electrode.

RGO films on ITO-PET were examined with a Carl Zeiss Ultra Plus field emission scanning electron microscope (FESEM) equipped with an energy dispersive X-ray spectrometer (EDXS).

3. Results and discussion

Electrodeposition of RGO films on ITO-PET electrodes from GO aqueous solutions resulted in very homogeneous coatings at relatively large scale, as illustrated in Figure 1a, where a 5 cm x 5 cm RGO deposit on ITO-PET electrode is presented. A FESEM image of the RGO film (Figure 1b) shows the individual RGO sheets, which have a broad size distribution, with lateral dimensions ranging from hundreds of nanometers to several microns. Despite the apparent film heterogeneity at the nanoscale, the RGO deposit is macroscopically uniform as given by the film transmittance in different regions (80 ± 1 %T at 550 nm). In order to test the performance of the RGO-coated ITO-PET electrodes in ECD, several viologen-based devices were fabricated using both uncoated and RGO-coated ITO-PET electrodes according to the schematic diagram depicted in Figure 1c. All the tested devices were built with RGO-coated ITO-PET electrodes with the same transmittance to ensure the same amount of RGO. The electrochromic mixture containing EtV^{2+} , the ionic liquid BMIBF₄ (as electrolyte) and hydroquinone (as redox mediator) dispersed in propylene carbonate was sandwiched between two identical ITO-PET (bare or

RGO-coated) electrodes separated by a spacer. Typical size of the electroactive area was 2.5 cm x 2.5 cm.

Color changes in viologen-based ECD are due to the first electrochemical reaction in Scheme 1. The dicationic form (EtV^{2+}) of the first redox pair is colorless whereas the reduced radical cation ($\text{EtV}^{\cdot+}$) is dark blue. The reversible color change from colorless to blue was observed in all the devices when a voltage difference ≥ 2 V was applied between the two ITO electrodes as a result of EtV^{2+} reduction at the cathode. From here on we will refer to the potential difference (in absolute values) applied between the two electrodes as the operational voltage of the devices.

The UV-Vis spectroelectrochemical response of identical EtV^{2+} ECD with bare and RGO-coated ITO-PET electrodes was investigated. Our initial aim was to probe whether the RGO film could act as an electrochemically stable protective barrier of ITO to enhance the ECD cycling stability, as previously reported for polyaniline films on RGO-coated quartz. Initially, ECD fabricated with both types of electrodes, bare and RGO-coated ITO-PET, exhibited very similar electrochromic performance in terms of optical contrast and switching response. Both ECD reached transmittance changes ($\Delta\%T$) of $\sim 55\%$ at 2 V applied voltage in less than 20 s. However, in the course of continuous voltage cycling tests between 0 and 2 V it was noted that RGO films were gradually depleting from the ITO surface. Photographs of a typical ECD after depletion of the RGO coating are displayed in Figure 2a and 2b in the bleached and colored states respectively. It can be seen that a frame of RGO film under the adhesive spacer remains whereas in the area exposed to the electrochromic mixture the film has come off.

This undesirable oxidative dissolution of RGO nonetheless caused a very interesting effect. In ECD where RGO depletion occurred, and hence the GO/RGO redox pair (depending on the applied voltage) was incorporated to the electrochromic mixture, higher optical contrasts were

achieved at a given voltage than in RGO-free ECD. The electrochromic response of ECD fabricated with bare and RGO-coated ITO-PET electrodes after RGO depletion is compared in Figure 2c and 2d, where current density and transmittance changes at 600 nm (wavelength of maximum contrast for the electrochromic pair $\text{EtV}^{2+}/\text{EtV}^{+}$) are plotted versus time during two consecutive potential steps between 1.5 and 0.0 V. The current density during the coloration (1.5 V) and bleaching steps (0.0 V) was higher for the ECD containing the GO/RGO redox pair in the solution phase. Differences in the optical contrast of both devices were even more remarkable, with $\Delta\%T$ at 600 nm of 27% and only 3% for the ECD with and without the GO/RGO redox pair respectively. Although at this voltage the switching speed is faster for the RGO-free ECD this is due to its lower optical contrast. At voltages high enough to drive the same transmittance changes in RGO-free ECD the switching times are comparable.

The different response of the two types of ECD at increasing applied voltages is illustrated in the sequence of photographs shown in Figure 3. Color switching was achieved at significantly lower applied voltage in the device with the GO/RGO redox pair in the solution phase resulting from surface RGO depletion. While the ECD with bare ITO-PET electrodes did not show noticeable color changes at voltages below 1.5 V, the device fabricated with RGO-coated ITO-PET electrodes already switched to a perceptible pale blue color ($\Delta\%T = 12\%$) at voltages as low as 1.25 V. This lower switching voltage was consistently found in several ECD ($n > 4$) fabricated with RGO-coated ITO-PET electrodes after inducing an accelerated oxidative dissolution of RGO (applying > 2.5 V for typically 2-3 minutes). However, when the applied voltage is gradually increased above a threshold value (1.7 V) both types of ECD start to show similar optical contrasts.

The voltage dependence of the optical contrast of ECD with and without the GO/RGO redox pair is highlighted in Figure 4. Changes in percent transmittance ($\Delta\%T$) for each type of device correspond to the difference between $\%T$ measured at 600 nm at the end of each 30s duration voltage step between 0 ($\%T_b$) and the different applied voltages ($\%T_c$). Figure 4 shows average $\Delta\%T$ values from three ECD of each type and the relative standard deviation is given by the corresponding error bars. It can be seen that ECD with dispersed GO/RGO starts displaying measurable color switching at voltages as low as 1.0 V whereas RGO-free devices require a 1.4 V voltage to exhibit comparable $\Delta\%T$ (3-5%). That is, the transmittance-voltage curve of GO/RGO-containing ECD is shifted to lower voltages by 300-400 mV in the 1.0-1.5 V range, which results in much higher optical contrasts at a same applied voltage for ECD fabricated with RGO-coated electrodes. At higher applied voltages the difference in the response of both types of ECD starts to decrease, leveling off at 2.0 V.

It is known that the GO/RGO redox couple exhibits an electrochromic response.²¹ Therefore, in order to rule out a possible contribution from the intrinsic electro-optical properties of GO/RGO to the electrochromic response of the ECD, we carried out spectroelectrochemical measurements of GO/RGO-containing ECD without the EtV^{2+} electrochrome. Since zero transmittance changes were measured in the voltage range of 0.6-2.0 V (Figure 2d), the higher optical contrast of GO/RGO-containing EtV^{2+} ECD cannot be explained by contribution from the GO/RGO electrochromism. Instead, the color switching at lower voltage indicates that the dispersed GO/RGO redox couple seems to be acting as a redox mediator of the electron transfer reaction of the electrochromic pair $\text{EtV}^{2+}/\text{EtV}^{+}$.

In order to corroborate the GO/RGO-facilitated electrochemistry of $\text{EtV}^{2+}/\text{EtV}^{+}$, the effect of GO concentration in the cyclic voltammetry of EtV^{2+} solutions was examined using a three-

electrode electrochemical cell. Figure 5 shows cyclic voltammograms (CV) of 9 mM EtV²⁺ at a Pt electrode in the same electrolyte solution as that in the ECD in the presence of increasing GO concentrations. All CV exhibit the two pairs of reversible redox peaks corresponding to EtV²⁺/EtV⁺ and EtV⁺/EtV⁰ electrochemical reactions. It can be seen that the redox peaks shift to more negative potentials upon addition of GO to the EtV²⁺ solution along with a significant increase of the current density of the reduction peaks. The CV reveal that upon reduction of EtV²⁺ in the presence of GO, the electrochemically generated EtV⁺ radicals undergo electron transfer with GO. This charge transfer interaction results in the reduction of GO and storage of electrons that can be used to further reduce the surface-confined EtV²⁺ and hence, the enhanced reduction current densities. Similar electron donation from viologen radicals to graphene²² and GO^{23,24} has been previously demonstrated as well as the use of the transferred electrons to reduce other species such as Ag⁺ ions to produce Ag silver nanoparticles on RGO.^{23,24} Overall, this superior electrocatalytic properties of RGO for the electrochemical reactions of a large number of inorganic and organic electroactive compounds are the base for the development of RGO-based biosensors.²⁵ To a lower extent, smaller family members such as graphene quantum dots (GQD) are also known to facilitate oxidation or reduction of some species (Ag⁺, H₂O₂)²⁶ and due to their charge transfer properties they have recently been proposed as alternative to conventional electrolytes in ECD of GQD-methyl viologen nanocomposites.²⁷

In summary, we have shown that solution-phase GO/RGO from oxidative dissolution of RGO-coated electrodes acts as an electron mediator facilitating the EtV²⁺/EtV⁺ redox reaction and consequent color switching, thus enabling ECD with lower operational voltage.

Conclusions

Flexible EtV²⁺ ECD have been prepared using ITO-PET electrodes and ITO-PET coated with a RGO film electrodeposited from GO aqueous solutions. The electrochromic response of ECD with bare ITO-PET and RGO-coated ITO-PET electrodes has been examined in the search of higher cycling stability for the RGO-coated electrodes. Initially both types of ECD exhibited comparable optical contrast and switching times. However, a gradual oxidative dissolution of the RGO film occurred in the course of continuous voltage cycling tests. As a result, GO/RGO was incorporated to the electrochromic solution, leading to ECD where color switching was achieved at lower applied voltages than in the GO/RGO-free devices. This electron mediator property of the GO/RGO redox couple in the electrochemical reaction of the electrochromic system EtV²⁺/EtV⁺ enabled ECD with higher optical contrast at a certain applied voltage. A possible contribution from the intrinsic electrochromic response of the GO/RGO redox couple was ruled out. These findings can be inspiring in the design of other types of ECD with lower operational voltage, thus avoiding undesired degradation or side-reactions, by incorporation of graphene-like materials with electrocatalytic properties to the electrochromic layer.

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Figure Captions

Figure 1. (a) Photograph of a RGO film electrodeposited on ITO-PET and (b) corresponding FESEM image showing the individual RGO sheets. (c) Schematic of the ECD assembly with the EtV^{2+} containing electrochromic mixture sandwiched between two RGO-coated ITO-PET electrodes.

Figure 2. Photographs of an EtV^{2+} ECD after depletion of the RGO film from the ITO surface in the bleached (a) and colored state (b). Current density (c) and transmittance changes at 600 nm (d) measured during chronoamperometric potential steps between 1.5 and 0.0 V for EtV^{2+} ECD fabricated with bare (black) and RGO-coated (red) ITO-PET electrodes. Response of a device with RGO-coated ITO-PET electrodes and no EtV^{2+} present (dotted line).

Figure 3. Photographs of EtV^{2+} ECD with the same composition fabricated with RGO-coated ITO-PET (left images) and bare ITO-PET electrodes (right images) at the applied voltages indicated in the figure.

Figure 4. Transmittance changes at 600 nm at different applied voltages for several EtV^{2+} ECD fabricated with bare (black) and RGO-coated ITO-PET (red) electrodes. Transmittance values were taken at the end of each 30 s switching step between 0 V and the indicated voltages.

Figure 5. CV of 9 mM EtV^{2+} at a Pt electrode in a polycarbonate solution containing 2M BMIBF_4 and 9 mM HQ at a scan rate of 50 mV s^{-1} (dashed line). Solid lines show CVs recorded in the presence of 1.3, 1.9, 2.6 and $3.2 \mu\text{g mL}^{-1}$ of GO, respectively (in the direction indicated by the arrow).

Scheme 1. Electrochemical reactions responsible for color changes in EtV^{2+} based ECD

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Abstract Graphic

