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Interfacial redox centers as origin of color switching in organic electrochromic device

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ABSTRACT

In an attempt to understand the color switching mechanism of organic electrochromic devices, live spectroscopy of a viologen based device has been done. Role of redox reactions taking place at the electrode/electrolyte interface has been identified using Raman and UV–Vis spectroscopies carried out during the device operation. In-situ Raman and transmission/absorption studies establish the origin of bias induced color change, between a transparent and navy blue color, in the electrochromic device. The origin of color change has been attributed to the bias induced redox switching between its dication and free radical forms which have different optical properties from each other. Raman spectra collected from negative and positive electrodes of the device reveal that blue color species (free radical) are present at the negative electrode which is created due to reduction of the dicationic form. In-situ UV–Vis spectra reveals that the navy blue color of the device under biased condition is not due to increase in the transparency corresponding to the blue wavelength but due to suppression of its transparency corresponding to the complementary colors as studied using a from CIE (Commission Internationale de l'Eclairge International Commission on Illumination) chart. Absorption modulation has been reported from the device with good ON/OFF contrast of the device.

1. Introduction

An electrochromic device, as name suggests, is a device which changes color as a result of an electrical bias. This phenomenon of bias induced color change, called electrochromism, was first observed in the nineteenth century [1]. Electrochromism has been studied in recent times because of many applications in science and technology [2–5]. Detailed reviews are available in the literature about electrochromic effects from different chemicals and materials [2,6]. Electrochromic effects are observed as a result of redox processes either in a solid-state device or in an electrochemical cell. Origin of this property lies in the fact that many materials show multiple redox states with different optical properties (e.g. absorption spectra). Different electrochromic materials are used as the active material, which could be in the form of metal oxide like tungsten oxide [7] or a cationic molecule [8–10].

One particularly intriguing class of materials in this context is bipyridinium species, which are formed upon *N*,*N*-diquaternization of 4,4′- bipyridine, also known as viologens. An example of such a viologen molecule is shown in Scheme 1. Viologen is an organic compound for potential use in flexible electrochromic devices due to its activity in reversible redox reaction and excellent electron accepting nature. In other words, Viologens, are reducible materials used in solid-state electrochromic devices, which may undergo one- or two-electron reductions [9,11–14]. Ease of processing and use have stimulated intensive research into the electrochromic properties of viologens. The current research was undertaken to better understand viologen electrochromism and to simplify the device design for realization of a solid-state electrochromic device.

Controlling the often complex stoichiometry of metal oxides is a complication when fabricating electrochromic devices based on these materials [15,16]. In addition, many metal oxides lack sufficient transparency for use in a wide range of applications. In contrast, viologen based materials are solution processable and can yield flexible electrochromic devices. In order to achieve an electrochromic response in the solid state, an ionically conducting matrix is required as well as a redox counter-reaction.

Very recently, lithium perchlorate in polyethylene oxide (PEO)

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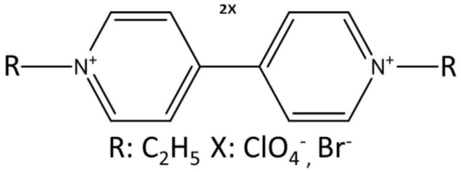

Scheme 1. Ethyl Viologen molecule.

has been used successfully as a solid electrolyte for organic electronics in general and thin film transistors in particular [10,17–21]. Ethyl viologen in PEO matrix can be a good choice for making viologen based electrochromic devices, at least for testing purposes. Ethyl viologen diperchlorate ($EV(ClO_4)_2$) can be a good candidate because it contains EV^{2+} which is a good electron acceptor and also contains perchlorate ion which can act as electrolyte. Its solution in an appropriate solvent is transparent and does not absorb visible light until gets reduced to radical cationic form $EV^{\bullet+}$ after accepting an electron. In the reduced state it shows absorption peak at 396 and 606 nm which indicates blue color of the device [22]. Radical cations play an important role in the optical property of any material. Some molecules do not show any absorption in the visible region but its free radical exhibits higher absorption in this wavelength rage [23]. Viologen is one of them which show absorption in its radical cationic state and due to this it makes viologen eligible to be categorized as an electrochromic material [24]. Radical cation of viologen can be obtained by chemical, electrical and optical methods and are sensitive to environment [25]. The advantage with viologen is that it shows reversible switching between the two oxidation states mentioned above. In other words, $EV^{\bullet+}$ can go back to EV^{2+} by oxidation, which shows no absorption in the visible region which is transparent state of the device. Details of redox reactions taking place during oxidation and reduction of EV have been provided in SI separately. A solid state electrochromic device can be made using viologen by appropriately controlling the redox process using an electric bias.

In the present work a simple electrochromic device has been fabricated in two geometries to study the fundamental reason of color change by in-situ UV–Vis and Raman spectroscopies. A clear understanding may enable one to get other colors than blue. In depth studies have been done by observing bias induced changes in EV species using spectroscopic techniques in-situ. The in-situ experiments help in understanding the underlying mechanism for bias induced color change which is required for making a versatile electrochromic device. Nondestructive spectroscopic techniques like Raman and UV–Vis may prove to be handy in analyzing the mechanism for the same. The two geometries used to understand the bias induced color change enables us to carry out in-situ measurements for an in-depth analysis. In the simplest geometry, the EV (in an appropriate matrix) has been sandwiched between two Indium Tin Oxide (ITO) electrodes on quartz substrate to get the device in cross-bar geometry (CBG). Similar device was fabricated by drop casting EV in between two gold electrodes separated by few microns where both the electrodes are on the same plane. Schematic, to show both the geometries, have been shown in Fig.S1 in supplementary information (SI). Open face geometry (OFG) device is used for in-situ Raman spectroscopy with electrical circuit arrangement to see the molecular change by applying bias. Raman spectroscopy experiments in OFG device and result clearly revealed connection between electrochemical doping and Raman peak position. Both UV–Vis and Raman spectroscopic data reconcile the correlation between charge carriers and color changes in viologen base devices. The free radical cation has been depicted as the fundamental charged species responsible for the color changing properties in ethyl viologen. Appropriate control experiments have been carried out to validate the conclusions.

2. Experimental details

Commercially available chemicals from Alfa Aesar and Sigma Aldrich were used for preparing samples in the present study. Polyethylene oxide (PEO, Alfa Aesar, MW = 100 000), Ethyl viologen diperchlorate (98%, Sigma Aldrich), Sodium borohydride ($NaBH_4$, Alfa Aesar), and Acetonitrile (ACN, anhydrous, 99.8%, Sigma Aldrich) were used as received.

Active material used for fabricating electrochromic devices was prepared in the solution form by mixing 4 wt% ethyl viologen diperchlorate [$EV(ClO_4)_2$] in acetonitrile and 5 wt% PEO in acetonitrile. The PEO solution was filtered through a 0.45 μm PTFE filter before adding the viologen solution. The solution (PEO+EV) has been deposited over the electrode by dropping 3 μl of solution in such a way that the drop centers on the E_1-E_2 gap in the OFG (Fig. S1 in SI) and then dried the film in vacuum.

Cross-bar geometry (CBG) device has been fabricated by placing a film of EV+PEO between two transparent conducting electrodes of ITO deposited on quartz substrate using magnetron sputtering deposition [26]. The EV+PEO film was obtained on an ITO coated substrate using spin coating. After spin coating, second ITO electrode was laminated face to face on the spin coated substrate. The extreme part of both the electrodes was painted by silver glue for making connection with external power supply. UV–Vis spectroscopy was performed using Cary 60 UV–Vis spectrophotometer of Agilent whereas Raman spectroscopy was done using LABRAM HR spectrometer using a 633 nm excitation source.

3. Results and discussion

Fig. 1 is the combined pictorial representation of internal and external mechanism of CBG device. Fig. 1(a) shows cross sectional schematic view of CBG device with its biasing arrangement. Fig. 1(b) is corresponding actual photographs of CBG device on various voltages. Fig. 1(c) corresponds to proposed model which shows molecular dynamics and redox reaction within the device as a result of applied bias. Fig. 1(a) shows that when external potential is 0 V, device is in its OFF state which corresponds to the transparent state and thus 'IITI' can be seen through the device clearly in Fig. 1(b). The transparency of the complete device reduces and becomes opaque after the application of −3.5 V bias as shown in Fig. 1(b). Color change in viologen is a well reported phenomenon [27] and is often assigned to the different absorption/transmission properties exhibited by viologen species in its different oxidation states. Typical optical properties of chemically reduced viologen show that blue color originates due to the presence of $EV^{\bullet+}$ species which can be obtained by chemically reducing EV^{2+} (present in ethyl viologen diperchlorate) which is transparent. Alternatively, similar redox change can be induced in the material in the form of a solid state device as a result of electrical bias which provides the basis for an electronic electrochromic device.

Mechanism responsible for bias induced color change as shown in Fig. 1(b) can be understood as follows, when we apply negative potential on the device, current starts flowing through the device and exchange of electron takes place. Electrons are injected from the electrode which is connected with the positive terminal of the battery, due to this viologen molecules which are nearer to this electrode get reduce. By the formation of $EV^{\bullet+}$, which shows higher absorption of green color, will make the device opaque (ON) for this color window near the interface. EV^{2+} and ClO_4^- species (in PEO matrix) are randomly distributed in between the two ITO electrodes in the absence of bias (V = 0). When bias is applied