Electrochromic response, structure optimization and ion transfer behavior in viologen adsorbed titanium oxide films

Shweta Bhandari, M. Deepa, A.K. Srivastava, S.T. Lakshmikumara, RamaKant

Nanostructured TiO₂ films have been fabricated using a simple wet chemistry route and the post-deposition annealing temperature has been optimized on the basis of crystal structure, particle and pore size, reflectance (diffuse) and band gap. The film annealed at 700 °C with a rutile structure, equipped with mesopores of 15 to 30 nm dimension, high diffuse reflectance ($R_{\text{diffuse}} = 91\%$) and an indirect band gap of 2.5 eV was found to be most suitable for the adsorption of bis-(2-phosphonoethyl)-4,4′-bipyridinium dichloride (viologen). The electroactive behavior of the viologen adsorbed TiO₂ film as a function of reduction level and in oxidized and neutral states has been followed by cyclic voltammetry and electrochemical impedance spectroscopy through equivalent circuits and compared with the response of blank TiO₂. It has been shown that interfacial charge transfer resistance governs ion intercalation during coloration with little contribution from the charge transfer and double layer capacitive components. The remarkable coloration efficiency (203 cm² C⁻¹, λ = 720 nm) and good reversibility of the color-bleach process for viologen adsorbed TiO₂ films have been found to be closely linked to the microstructure of the oxide layer.

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1. Introduction

Electrochromic materials offer simple means to modulate solar radiation by application of an electric voltage or current, thereby rendering them attractive as electrodes in energy efficient windows and dynamic displays [1-3]. A vast number of electrochromic materials find utility in such electrochromic devices. Of the lot, the salts of quaternized 4,4′-bipyridine, commonly known as viologens came into focus as one of the active components of electrochromic devices [4,5], because of their brilliant color and the possibility of tuning different colors by designing substituted viologen molecules. In electrochromic devices (rear view mirrors, displays and windows) even to this date, the traditional approach involves the incorporation of the viologens into the device in solution phase [6,7]. Recently, viologen modified nanostructured semiconductor electrodes [8-12] have been found to be a promising alternative for tunable modulation of transmission/reflection of solar radiation.

The nanostructured semiconductor most widely used for adsorption of viologens/dye is titanium oxide (TiO₂) owing to its high surface affinity towards certain ligands, intercalation properties, tunability of the conduction band and high reflectance [11-14]. TiO₂ is a wide gap semiconductor material (-3.4 eV), existing mainly in two forms: anatase and rutile, which are thermodynamically stable at different temperatures. In particular, mesoporous TiO₂ nanocrystalline films [15] are of considerable interest as compared to their other counterparts. The mesoporous morphology coupled with high surface area enables a greater uptake of viologen molecules, thus leading to a higher contrast ratio and redox activity [16,17]. In the past self assembly of block copolymers, surfactants and colloids based on titanium alkoxides have been used extensively for fabrication of nanostructured TiO₂ films [18,19]. In this context, Grätzel and coworkers [20] produced nanocrystalline TiO₂ thin film electrodes with a broad pore size distribution and demonstrated the efficient utilization of the attributes of nano-TiO₂ for forming high performance dye sensitized solar cells. However, most of the syntheses of TiO₂ mesophases have entailed the use of solution chemistry to control porosity. Little work has been done on controlling the crystallinity and porosity of titania by a thermal treatment [21-23].

Furthermore, electrochromophore modified nanostructured TiO₂ films with optimized microstructure and crystal structure can allow a facile redox (ion) transfer between the electrolyte and the chemically tethered viologen as well as a rapid electron transfer from the conducting electrode to viologen through the mesopores of TiO₂. To this end, here we report the fabrication of nanostructured thin films of TiO₂ using a wet chemistry process. The evolution of grain and pore morphology as a function of post deposition annealing temperature has been studied by x-ray diffraction (XRD) and electron microscopy. On the basis of diffuse reflectance and transmittance in the visible and the near infrared (NIR) regions and optical band gap of these films, the film most suitable for anchoring viologens has been identified. The redox response, coloration efficiency and electrochemical impedance
of the nanostructured TiO₂ film with adsorbed viologens have been studied as these are the parameters which determine the practical utility of these films for electrochromic display applications.

2. Experimental details

2.1. Fabrication of nanostructured TiO₂ films

Titanium oxide films were prepared directly from the TiO₂ nanoparticles (Degussa, P 25). A colloidal formulation was obtained by sonicating TiO₂ nanoparticles (14–20 nm) in poly(ethylene glycol) 400 (Merck) (1:4 by weight) as the medium. The resulting homogenous white paste was spin coated on SnO₂:F coated glass substrates (Pilkington, sheet resistance ~14 Ω/sq, 4 mm thick with a soda lime glass base capable of withstanding high annealing temperatures) at 2500 rpm for 30 s to obtain TiO₂ thin films. The as-deposited films were annealed at 400, 450, 500, 600 and 700 °C respectively each for half an hour in air and the resulting films were stored in air. The thermal treatment imparted better adherence and chemical stability to the as-deposited films.

2.2. Synthesis of bis-(2-phosphonoethyl) 4,4′-bipyridinium dichloride

A reaction mixture containing 4,4′-bipyridine (2.2 g, Aldrich) and diethyl-2-ethyl bromophosphonate (7.5 g, Aldrich) was formed in 37.5 ml of deionized water (resistivity ~18.2 MΩ cm) and allowed to cool after refluxing for 40 h at 40 °C. This was followed by addition of 37.5 ml of concentrated hydrochloric acid (35%) and further refluxing for 15 h at the same temperature. The resulting mixture was then concentrated to 25 ml by heating in a water bath and ice cold isopropanol (Merck) was added drop wise forming off-white precipitates. Finally, the pure crystalline product of bis-(2-phosphonoethyl) 4,4′-bipyridinium dichloride was recovered after repeated washing with isopropanol and drying in air.

2.3. Formation of viologen modified TiO₂ films

A 0.02 M aqueous solution of bis-(2-phosphonoethyl) 4,4′-bipyridinium dichloride was used to incorporate the viologen into the TiO₂ film (annealed at 700 °C) via adsorption by placing the two in contact with each other for 24 h in a vacuum dessicator. The film was then washed with deionized water and dried in air.

2.4. Characterization

Thickness of the TiO₂ films was determined with S6P Mahr Perthometer. The thickness reduces from ~1.26 μm for the film annealed at 400 °C to ~0.85 μm for the film annealed at 700 °C. XRD patterns of the films were recorded in the 2θ range from 11 to 70°, with a Bruker AXS D8 advance diffractometer, using CuKα radiation (λ = 1.5405 Å). A scanning electron microscope (LEO 440 SEM) was employed for studying the surface morphology. Transmission electron microscopy (TEM, FEI CM12) was employed for examining the microstructural features of the films. FTIR spectra for the films were recorded in reflection mode with a Perkin Elmer Spectrum BX FTIR spectrophotometer; the angle of incidence was kept at 35°. The transmittance (T) and reflectance (R) spectra for samples annealed at different temperatures were recorded in the 300–2000 nm wavelength range in a UV-3101 PC Shimadzu spectrophotometer. For reflectance measurements, an integrating sphere of 60 mm diameter was employed as the samples showed only diffuse reflectance and negligible specular reflectance; the angle of incidence was fixed at 8°. Cyclic voltammetry (CV) for the TiO₂ film (annealed at 700 °C) and viologen modified TiO₂ films were performed in a classical three-electrode electrochemical cell on an Omni Potentiostat (Cypress instruments), wherein an Ag/Ag⁺ was employed as the reference electrode and a Pt rod was used as the auxiliary electrode in a liquid electrolyte (1 M lithium perchlorate (LiClO₄)-propylene carbonate (PC)). Impedance studies were carried out in the same three-electrode cell configuration on a CH electrochemical analyzer. Impedance spectra were fitted using Z-view software. Absorbance (A) spectra for colored and bleached viologen modified TiO₂ films (annealed at 700 °C) were recorded in-situ in a glass cell (40 mm × 40 mm × 10 mm) in the 300–1100 nm wavelength range in a Perkin Elmer Lambda 25 spectrophotometer. The films were colored under different reduction potentials varying from ~0.75 to ~1.5 V with respect to a Ag/Ag⁺ reference electrode for a fixed duration of 60 s in liquid electrolyte (1 M LiClO₄-PC).
3. Results and discussion

3.1. Phase formations and microstructural investigation of TiO$_2$ films

The XRD patterns of TiO$_2$ thin films annealed at 400, 450, 500, 600 and 700 °C respectively are displayed in Fig. 1. A significant narrowing of Bragg peaks has been observed with increasing annealing temperature indicative of increase in crystallinity and grain size. The diffractogram of the film annealed at 400 °C (Fig. 1A) shows well resolved diffraction peaks at interplanar spacings of 3.54, 1.89 and 1.66 Å corresponding to the (101), (200) and (211) characteristic reflections of the anatase phase of TiO$_2$ in accordance with the PDF number 21-1272 from the ICDD library of the spectra. A low intensity peak at $d = 3.26$ Å ($hkl = 110$) arises from the rutile component of TiO$_2$ as per PDF number 21-1276. With an increase in annealing temperature, the diffraction peaks corresponding to anatase phase attenuate, while the diffraction peak corresponding to the (110) plane of the rutile phase starts to intensify progressively (Fig. 1B–D). At 700 °C the film shows diffraction peaks corresponding to the rutile phase having characteristic reflections along (101), (111), (211) and (002) planes with preferred orientation along (110) (Fig. 1E). The observed phase change from anatase to rutile with annealing temperature is in agreement with several reports [24–26] on TiO$_2$ films/bulk.

FTIR spectra of the films are shown in Fig. 2. The band at 834 cm$^{-1}$ observed in the spectrum of the film annealed at 400 °C can be assigned to the LO vibrational mode of the Ti-O bond [27,28]. However, this band downshifts to 786 cm$^{-1}$ at 700 °C due to anatase to rutile conversion. The other peaks at 622 cm$^{-1}$ and 934 cm$^{-1}$ appearing in the spectrum of the film annealed at 700 °C correspond to the short-range order of the octahedrally coordinated Ti-O bond and $\nu$(Ti-O) stretch frequency in rutile structure [25,29].

The surface morphology of the annealed TiO$_2$ films shown in Fig. 3 reveals a continuous granular and porous surface morphology, resulting from the (i) surfactant properties of poly(ethylene glycol) PEG and (ii) the annealing treatment. The choice of PEG as the medium...
for dispersing TiO₂ nanoparticles stems from its capability to form a smooth homogenous formulation of TiO₂. Further, its ability as a surfactant to impart good wetting characteristics to the precursor solution effectively manifests in the formation of uniform, well adherent TiO₂ films [30,31]. The micrographs highlight the macroporous character of the film surface. The pore size decreases continuously with increase of annealing temperature from 400 to 700 °C. Abutting feature of grains and the sub-micron sized cracks on the film surface are observed at 400 and 450 °C (Fig. 3A and B) and these become less prominent at higher temperatures. The stresses generated in the film due to an uncontrolled rate of evaporation of the organics from the film during thermal treatment are responsible for the observed cracks. But at 700 °C, since there are no remnant organics as the boiling point of PEG lies in the range of 250–280 °C; only densification and grain growth occur that cause a shrinkage of the observed cracks. A few coarse grains with distinct boundaries can be perceived from the image of the film annealed at 700 °C (Fig. 3C).

TEM micrographs of the films annealed at various temperatures are displayed in Fig. 4. The microstructural examination of the samples annealed at 450 °C (Fig. 4A) reveals a network of mingling grains and mesopores and the glazy contrast of the micrographs indicate the low crystallinity of the samples at these temperatures. The pore and grain size distribution is narrow and lies between 20 and 40 nm. At 500 °C, the grains are well developed with dimensions of about 30–50 nm (Fig. 4B). The pores are now randomly distributed and the mesopore size varies between 20 and 40 nm. Densification occurs as the temperature is raised to 600 °C, along with the formation of elongated pores, 10 to 30 nm in size; the observed pore shrinkage is a direct manifestation of annealing at elevated temperatures. Grain coalescence is also activated at higher temperatures, as agglomerates 60 to 70 nm in diameter are also observed in some regions of this film (Fig. 4C). Porosity is retained even upon annealing the film at 700 °C (pore size ~15 to 30 nm) (Fig. 4D). This film is composed of well-separated distinct grains with well-defined grain boundaries, which affirms that the film is highly crystalline at this temperature. The faceting around individual grains reflect further about the growth of TiO₂ along certain preferred crystallographic planes of the rutile crystal structure. The most preferred planes from the XRD (Fig. 1E) may be attributed to (110), (101) and (211). Phase transformation in TiO₂ induced by annealing is also evident from the electron diffraction patterns and these observations are in agreement with XRD measurements.

3.2. Optical properties of pristine TiO₂ films

Transmittance and diffuse reflectance spectra of the annealed films of TiO₂ in the 300–2000 nm wavelength region are illustrated in Fig. 5. For films annealed at 450, 500 and 600 °C (Fig. 5A), the transmittance shows a continuous increase with wavelength up to 1250 nm with maximum transmittance (Tmax) ~50–55% observed in the near infrared (NIR) region which is then followed by a further decrease at longer wavelengths. The highest value of Tmax (~55%; λ=1559 nm) is observed for the film annealed at 600 °C. The wavelength for Tmax shows a red shift for the films annealed at 600 and 700 °C as compared to films thermally treated at lower temperatures. This could be related to the emergence and the subsequent preponderance of the rutile phase at 700 °C whereas the films annealed at lower temperatures (≤500 °C) are characterized by a dominant anatase phase [25]. The observed red shift can also be described as a result of nanoparticle aggregation and increased grain size with increase in annealing temperature [32].

In concordance with the large transmittance in the NIR region, the diffuse reflectance of these films is high in the visible region, as the films show low transmittance in this region (Fig. 5B). Again, for all
films of TiO₂ annealed at different temperatures, reflectance increases as a function of wavelength, shows a sharp peak in the visible region (~410–430 nm) and then declines gradually regardless of the annealing temperature. The highest magnitude of reflectance maximum (Rₘₐₓ ~91% at 422 nm) is shown by the film annealed at 700 °C. Rₘₐₓ is nearly of the same magnitude (~65% at 410 nm) for the films annealed at 400, 450, and 600 °C. The lowest value of Rₘₐₓ is exhibited by the film annealed at 500 °C (~47% at 400 nm). Beyond Rₘₐₓ, while reflectance decreases monotonically for films annealed at 400, 600 and 700 °C, the reflectance of the films annealed at 450 and 500 °C shows a steady increase from 1360 nm onwards. According to the Drude theory, the different free electron scattering mechanisms in crystalline oxides control reflectance [33]. Particle size effects therefore govern electron scattering in TiO₂ and consequently NIR reflectance trends change with annealing temperature. The information regarding the electronic band structure of the annealed samples is inferred from the band gap values. The absorption coefficient (α) was determined using

\[ \alpha(\lambda) = \log \left( \frac{1}{1-R(\lambda)/T(\lambda)} \right)/d \]  

(1)

and α is related to the energy (hν) of incident photon by the relation,

\[ \alpha = (hν-E_g)^{n}/hν \]  

(2)

where, hν is the photon energy and n = 1/2 for an indirect optical band gap (E_g) and n=2 for a direct optical band gap. The latter corresponds to phonon-assisted transitions. In TiO₂, the direct forbidden transition is weak and the indirect allowed transition prevails in the optical absorption just above the absorption edge [34]. Furthermore, it is also known that in transition metal oxides the indirect transitions predominate in amorphous films or in films with low crystallinity (as in films annealed at temperatures ≤500 °C) whereas direction transitions are more pronounced in polycrystalline films (similar to films annealed at temperatures ≥600 °C). The direct and indirect transitions between the 2p valence band of oxygen and 3d conduction band of titanium are evident from the plots of the hν and (αhν)^2 and hν and (αhν)^1/2. Extrapolation of the absorption edge to zero in these curves furnished the values of respective optical band gap of the annealed films.

![Fig. 5](https://via.placeholder.com/150)

**Fig. 5.** Transmission (A) and reflectance (B) spectra of the films annealed at (a,a') 400 °C, (b,b') 450 °C, (c,c') 500 °C, (d,d') 600 °C and (e,e') 700 °C in the 300–2000 nm wavelength region.

In our case, the indirect and direct optical band gaps displayed in Fig. 6A and B, increase on raising the temperature from 400 to 500 °C; from 2.4 to 2.6 eV and from 3.07 to 3.11 eV, respectively. Further increase in temperature causes optical band gap narrowing, corresponding to both indirect and direct transitions. This is a natural consequence of increasing grain size, degree of crystallinity and the accompanying phase transition from anatase to rutile. Indirect optical band gap reduces to 2.4 eV and direct gap lowers to 2.85 eV for the film at 700 °C. It is presumed that the distortions and tilting of TiO₆ octahedra become more prominent, as the temperature is raised from 500 to 700 °C and are responsible for the drop in the E_g value. This is in agreement with the reported optical gaps of 2.18 and 2.65 eV by Nagaveni et al. [35] for crystalline TiO₂. As compared to the films annealed at 500 °C (E_g(indirect)=2.6 eV, E_g(direct)=3.11 eV), which exists predominantly in the anatase phase, there is a narrowing of optical band gap for the films annealed at 700 °C, wherein the rutile phase preponderates. This concurs well with the reported drop in optical gap with change in crystal structure of TiO₂ from anatase to rutile [35]. The influence of crystalline structure of TiO₂ on the optical gap is also evident from the anomalous trend of E_g (direct/indirect) plots vs. hν for the film annealed at 700 °C. The curve is distinctly different for this film with a substantial rutile component from that observed for films annealed at other temperatures.

Amongst all, the film annealed at 700 °C exhibits the highest reflectance in the visible region and this is suggestive of its suitability for electrochromic displays as no additional reflecting layer is required. That this film is also characterized by the lowest E_g ~2.4 eV (among all) is advantageous for its use in devices. This prompted us to use these films for viologen adsorption and further investigation of the electrochemical and optical behavior of the modified film as an intercalation cathode. Moreover, since the film continues to be porous
and B. For the pristine TiO$_2$ and 2.3 mC cm$^{-2}$ higher than that of bare TiO$_2$ function of different scan rates of 10, 20, 50 and 75 mV s$^{-1}$ observed in viologen modiﬁed TiO$_2$ demonstrating that a greater number of charges are involved in the magnitudes of current density maxima are also much larger, thus in both anodic and cathodic branches of the voltammogram and the.

The electrochemical behavior of the viologen modiﬁed TiO$_2$ film annealed at 700 °C and viologen modiﬁed film have been analyzed in 1 M LiClO$_4$-PC in the frequency range of 10 MHz to 100 kHz in Fig. 9. A range of DC potentials 0, −0.5, −1.0, −1.5 and +1.5 V were super-imposed on a ﬁxed 5 mV AC amplitude. The typical Nyquist plot as shown in Fig. 9A at 0 V of viologen modiﬁed TiO$_2$ film consists of three parts: two semicircles in the high frequency region of 100 kHz to 664 Hz and 664 Hz to 0.4 Hz followed by a linear behavior in the lower frequency region below 0.4 Hz. The equivalent circuits corresponding to these plots which gave best ﬁts to the experimental data points over the entire frequency range are shown in Fig. 10. The Z-view impedance software was used for ﬁtting the impedance curves and the values of corresponding components are listed in Table 1. The error of the ﬁts for the different spectra was in the range of 5–20%. The error level is slightly on the higher side in some cases, as the system herein tends to digress from the ideal behavior. The half semicircle is due to the solution resistance and polarization of the electrolyte ions containing $R_q$ and $C_p$ respectively as can be seen from the insets of Fig. 9(A–C). From the same insets the normal double layer electrochemical capacitances (as found for a blocking electrode in an electrolyte) are 8.0×10$^{-8}$ F (0 V), 3×10$^{-8}$ F (−0.5 V) and 1.6×10$^{-8}$ F (−1.0 V). At 0 V, $C_p$ is lowest, as there is only the AC sinusoidal voltage but no driving DC voltage to induce charge separation and at ﬁnite DC potentials, the $C_p$

![Fig. 7. Cyclic voltammograms of (A) pristine TiO$_2$ film annealed at 700 °C and (B) same with adsorbed viologen in a 1 M LiClO$_4$-propylene carbonate liquid electrolyte at 100 mV s$^{-1}$.

Even upon annealing at such a high temperature, this permits the uptake of a large number of viologen molecules, as will be seen in the following section.

3.3. Electrochemical behavior of viologen adsorbed TiO$_2$ films

On adsorbing viologen on TiO$_2$ film annealed at 700 °C via its aqueous solution, an effective charge transfer complex formation occurs by interaction between Ti$^{4+}$ metal ions and the negatively charge phosphonate ions on the viologen molecules. The electrochemical activity of the TiO$_2$ film prior to viologen adsorption and after viologen incorporation in the film matrix can be viewed in Fig. 7A and B. For the pristine TiO$_2$ film (Fig. 7A), only a single distinct cathodic peak is observed at −0.60 V with a current density maximum of 0.2 mA cm$^{-2}$ ascribable to the reduction of TiO$_2$ [36] as follows:

$$\text{Li}_x\text{TiO}_2\rightarrow\text{TiO}_2 + x\text{Li}^+ + xe^{-}.$$  \hfill(3)

However, for the film with adsorbed viologen, peaks are observed in both anodic and cathodic branches of the voltammogram and the magnitudes of current density maxima are also much larger, thus demonstrating that a greater number of charges are involved in the oxidation–reduction of this film. The maximum current density ($i_{\text{max}}$) observed in viologen modiﬁed TiO$_2$ film is 0.5 mA cm$^{-2}$ which is higher than that of bare TiO$_2$ film ($i_{\text{max}}=0.2$ mA cm$^{-2}$). At 100 mV s$^{-1}$, the charges inserted and extracted in a viologen modiﬁed ﬁlm are 3.2 and 2.3 mC cm$^{-2}$ respectively, with a ratio of 1:4. In the cathodic cycle, the peak at −0.1 V corresponds to the formation of the viologen radical cation, a blue colored complex and the peak at −0.3 V in the anodic cycle indicates the formation of neutral viologen, which is colorless. The electrochemical behavior of the viologen modiﬁed ﬁlm as a function of different scan rates of 10, 20, 50 and 75 mV s$^{-1}$ respectively is shown in Fig. 8. As can be observed in the Fig. 8, the different redox peaks begin to appear on increasing the scan rate. It is noteworthy that no such distinct peaks were observed by Canadas et al. [37] for similar films where TiO$_2$, was grown by a different method. At the lowest scan rate of 5 mV s$^{-1}$, no distinct peak is visible and current shows only a plateau like behavior indicating that at lower scan rates, capacitance dominates (as capacitance $\propto$ 1/scan rate) and therefore the redox behavior is not evident. But, at higher scan rates redox activity is seen and capacitance increases exponentially as a function of scan rate (in the range of 10–75 mV s$^{-1}$). The oxidation peaks increase in amplitude and shift to more positive potentials as sweep rate is increased from 5 to 100 mV s$^{-1}$ as a part of the total applied potential is consumed by solution resistance and it is increasingly so at higher scan rates. The linear variation of oxidation peak current densities with scan rate indicates a diffusion controlled reaction. The average value of the diffusion coefﬁcient as calculated by the Randles Sevčik equation is 0.34×10$^{-8}$ cm$^2$ s$^{-1}$. Since oxidation and reduction of the viologen occur on the white titania surface, the corresponding optical contrast renders the ﬁlm most suitable for electrochromic display applications. Moreover, we observed this color transition between white and purple to be reversible for about 50 cycles, which again shows that the viologens remain chemically anchored to the nanostructured titania surface.

The electrochemical impedance response of the blank TiO$_2$ film annealed at 700 °C and viologen modiﬁed ﬁlm have been analyzed in 1 M LiClO$_4$-PC in the frequency range of 10 MHz to 100 kHz in Fig. 9. A range of DC potentials 0, −0.5, −1.0, −1.5 and +1.5 V were super-imposed on a ﬁxed 5 mV AC amplitude. The typical Nyquist plot as shown in Fig. 9A at 0 V of viologen modiﬁed TiO$_2$ film consists of three parts: two semicircles in the high frequency region of 100 kHz to 664 Hz and 664 Hz to 0.4 Hz followed by a linear behavior in the lower frequency region below 0.4 Hz. The equivalent circuits corresponding to these plots which gave best ﬁts to the experimental data points over the entire frequency range are shown in Fig. 10. The Z-view impedance software was used for ﬁtting the impedance curves and the values of corresponding components are listed in Table 1. The error of the ﬁts for the different spectra was in the range of 5–20%. The error level is slightly on the higher side in some cases, as the system herein tends to digress from the ideal behavior. The half semicircle is due to the solution resistance and polarization of the electrolyte ions containing $R_q$ and $C_p$ respectively as can be seen from the insets of Fig. 9(A–C). From the same insets the normal double layer electrochemical capacitances (as found for a blocking electrode in an electrolyte) are 8.0×10$^{-8}$ F (0 V), 3×10$^{-8}$ F (−0.5 V) and 1.6×10$^{-8}$ F (−1.0 V). At 0 V, $C_p$ is lowest, as there is only the AC sinusoidal voltage but no driving DC voltage to induce charge separation and at finite DC potentials, the $C_p$

![Fig. 8. Cyclic voltammograms of viologen adsorbed TiO$_2$ film recorded at different scan speeds of 10, 20, 50 and 75 mV s$^{-1}$ in a 1 M LiClO$_4$-propylene carbonate liquid electrolyte.](image-url)
is higher but follows no systematic trend. $R_{CT}$, $C_T$ of TiO$_2$ and $C_{vio}$ of viologen combine to produce the second skewed semicircle corresponding to charge transfer impedance. As both the capacitances are controlled by one potential consequently they are connected in parallel [37] in the Randles equivalent circuit shown in Fig. 10A. This is the region which mainly controls the redox behavior of the electrode. The lower frequency region containing the diffusion controlled element, Warburg ($Z_W$) ideally, gives rise to a straight line inclined at an angle of 45° to the real axis, but here at 0 V, the impedance first slightly curves over to reach the real axis and then deviates away from it making an angle of 55° with respect to abscissa. Due to the finite surface roughness of the electrode the diffusion behavior deviates from the ideal one [38]. On applying a negative potential of −0.5 V, the drop in the value of charge transfer impedance is the first noteworthy feature and it continues to decrease on further increase of reduction potential (Fig. 9 B and C). When no DC potential is applied to the cell, the real component of charge transfer impedance ($R_{CT}$) is the highest with a value of 2000 Ω. $R_{CT}$ shows a systematic decrease with applied potential; it reduces to 600 Ω (−0.5 V) and further to 200 Ω (−1.0 V) and to just 12 Ω at −1.5 V. At extreme −1.5 V (Fig. 9D), the dominant capacitive part in the bulk resistance (as the first semi-circle has wider spread and larger amplitude than the second one) and the low magnitude of the charge transfer impedance confirm a facile redox transfer i.e. rapid charging and ingress of ions. Simultaneously, the charge injected also divides into TiO$_2$ and viologens to charge their respective capacitances [37]. Accordingly, the charge transfer
capacitance \( (C_{\text{Vio}}) \) decreases from 0.9 to 0.006 \( \text{F} \) as potential is raised from 0 to \(-1.5 \text{ V}\). Since it is the viologen, which is solely responsible for the reversible coloration in the film, the decrease in the magnitude of \(C_{\text{Vio}}\) is more significant for describing the redox process than the corresponding increase of \(C_{\text{Ti}}\), ongoing from 0 to \(-1.5 \text{ V}\).

When reverse bias potential of +1.5 \( \text{V} \) (Fig. 9E) was applied to the film, charge transfer impedance increases again \( (R_{\text{CT}}=42 \Omega) \) and \(C_{\text{Vio}}\) also increases to 0.6 \( \text{F} \) as compared to \(R_{\text{CT}}\) and \(C_{\text{Vio}}\) observed at \(-1.5 \text{ V}\). The higher value of \(R_{\text{CT}}\) at +1.5 \( \text{V} \) as compared to the \(R_{\text{CT}}\) at \(-1.5 \text{ V}\) indicates that the system is more efficient at reduction or coloration as compared to bleaching or oxidation. The high \(R_{\text{CT}}\) during oxidation could also be due to irreversible permanent trapping of some lithium ions. But the relatively lower values of \(C_{\text{B}}, C_{\text{Vio}}\) and \(C_{\text{Ti}}\) in comparison to \(R_{\text{B}}\) or \(R_{\text{CT}}\) irrespective of the magnitude of the applied potential) shows that the ion-diffusion in the film is governed by resistive rather than capacitive behavior.

In the blank TiO\(_2\) film (Fig. 9F) under \(-1.5 \text{ V}\), the absence of \(C_{\text{Vio}}\) is responsible for a lower value of capacitance \( (C_{\text{BT}}=2 \times 10^{-7} \text{ F}) \). The charge transfer impedance is also low \( (R_{\text{CT}}=42 \Omega) \) which is a proof of the fact that the mesoporous, nanocrystalline surface morphology of the blank TiO\(_2\) film is most conducive for lithium ion insertion. The CV response at the lowest scan rate (5 mV s\(^{-1}\)) can be compared with the impedance behavior at low frequency. The capacitive contribution in controlling the lithium insertion is evident from the Warburg region where the digression from the normal trend (45° w.r.t. abscissa) is seen under all potential conditions; the maximum deviation being at \(-1.5 \text{ V}\).

### Table 1

<table>
<thead>
<tr>
<th>Components of equivalent circuit</th>
<th>0 V (TiO(_2) + viologen)</th>
<th>(-0.5 \text{ V} ) (TiO(_2) + viologen)</th>
<th>(-1.0 \text{ V} ) (TiO(_2) + viologen)</th>
<th>(-1.5 \text{ V} ) (TiO(_2) + viologen)</th>
<th>(+1.5 \text{ V} ) (TiO(_2) + viologen)</th>
<th>(-1.5 \text{ V} ) (TiO(_2) blank)</th>
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<tbody>
<tr>
<td>(R_{\text{B}} ) (( \Omega ))</td>
<td>600</td>
<td>220</td>
<td>150</td>
<td>19</td>
<td>18</td>
<td>49</td>
</tr>
<tr>
<td>(C_{\text{B}} ) (( \text{F} ))</td>
<td>(8 \times 10^{-8})</td>
<td>(3 \times 10^{-8})</td>
<td>(1.6 \times 10^{-4})</td>
<td>(1 \times 10^{-5})</td>
<td>(1 \times 10^{-6})</td>
<td>(-)</td>
</tr>
<tr>
<td>(R_{\text{CT}} ) (( \Omega ))</td>
<td>2000</td>
<td>600</td>
<td>200</td>
<td>12</td>
<td>1600</td>
<td>42</td>
</tr>
<tr>
<td>(C_{\text{CT}} ) (( \text{F} ))</td>
<td>0.9</td>
<td>0.6</td>
<td>0.5</td>
<td>0.006</td>
<td>0.6</td>
<td>(-)</td>
</tr>
<tr>
<td>(C_{\text{Ti}} ) (( \text{F} ))</td>
<td>(2 \times 10^{-8})</td>
<td>(2 \times 10^{-6})</td>
<td>(2 \times 10^{-3})</td>
<td>(8 \times 10^{-3})</td>
<td>(2 \times 10^{-6})</td>
<td>(2 \times 10^{-7})</td>
</tr>
</tbody>
</table>

Fig. 10. Randles equivalent circuits of the viologen adsorbed TiO\(_2\) film at different DC potentials of (A) 0, \(-0.5, -1.0 \text{ V}\) and \(-1.5 \text{ V} \), (B) +1.5 \( \text{V} \) and (C) bare TiO\(_2\) film annealed at 700 °C at \(-1.5 \text{ V}\). \(R_{\text{B}}\) and \(C_{\text{B}}\) are the components for bulk movement of ions, \(R_{\text{CT}}\) is the charge transfer impedance, \(C_{\text{Ti}}\) is the capacitance of TiO\(_2\) film and \(C_{\text{Vio}}\) is the capacitance of viologen and \(Z_{\text{W}}\) is the Warburg impedance.

### 3.4. Optical behavior of viologen modified TiO\(_2\) films

The spectroelectrochemistry of the viologen modified TiO\(_2\) films in a 1 M LiClO\(_4\)-PC liquid electrolyte under different applied potentials of \(-0.75, -1.0, -1.25, -1.5 \text{ and } +1.5 \text{ V}\) is illustrated in Fig. 11. The absorbance spectra (Fig. 11A) in the wavelength region of 300–1100 nm show no observable peak at \(-0.75 \text{ V}\). But at \(-1.0 \text{ V}\), the film acquires a blue color and a pronounced absorption centered at about 800 nm is observed. In addition, a distinct sharp peak, though less intense is also observed at 380 nm under applied potentials \(\geq -1.0 \text{ V}\) along with the concomitant increase of absorption at 680 nm. On applying a negative potential, the surface bound dication of the viologen \(V^2+\) forms the radical cation \(V^+\) by gaining one electron from TiO\(_2\) and the appearance of the above two peaks at 380 and 680 nm is the consequence of \(V^+\) absorption [11].

The coloration efficiencies \( (\eta) \) i.e. the change in the optical density per unit charge density [33] as a function of wavelength for the viologen modified TiO\(_2\) films at different potentials by using the optical density obtained at \(+1.5 \text{ V}\) as reference are shown in Fig. 11B. Except for the film colored at \(-0.75 \text{ V}\), where coloration efficiency maximum is observed at 550 nm, at potentials \(\geq -1.0 \text{ V}\), the coloration efficiency maximum was found to lie in the range of 600–800 nm. The maximum coloration efficiency of 203 cm\(^2\) cm\(^{-1}\) (720 nm) is observed when the film was colored at \(-1.5 \text{ V}\). Incidentally, at this voltage, since the resistance to lithium intercalation is minimum (Fig. 9D), the enhanced absorbance change is explained. At \(-1.0 \text{ V}\) the maximum
coloration efficiency is 120 cm² C⁻¹ which is comparable to that reported by Cinnsealach et al. [11] for a viologen modified TiO₂ device. The values are much larger as compared to that of unmodified TiO₂ electrodes with reported values of ~2–22 cm² C⁻¹ [36,39].

4. Conclusions

Mesoporous, robust, nanocrystalline titanium oxide frameworks were obtained from a facile sol–gel spin coating method using a nanoparticle titania solution and subjected to annealing at different temperatures. The optimization of annealing temperature, i.e. 700 °C, on the basis of the film’s high reflectance in the visible region, rutile structure and porosity for viologen adsorption has been demonstrated. It has been shown that the resistive barrier at the viologen adsorbed TiO₂ film/electrolyte interface controls lithium ion insertion during reduction whereas the high and low frequency capacitances are less prominent. The mesoporous structure and high surface area of TiO₂ nanocrystallites is responsible for the facile redox transfer and it effectively translates into a large coloration efficiency maximum (203 cm² C⁻¹ at 720 nm) for the viologen adsorbed TiO₂ films. From the analyses, the suitability of viologen adsorbed TiO₂ films for high electrochromic contrast applications is evident.

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References