

Performance of chromophore-type electrochromic devices employing indium tin oxide nanorod optical amplification

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ABSTRACT

In this study, we used transparent and conductive indium tin oxide (ITO) nanorods, prepared through electron-beam evaporation onto ITO glass substrates, as electrodes for viologen-based electrochromic devices (ECDs). Although the shapes of these ITO nanorods could be controlled simply by manipulating the evaporation time, they always maintained their high optical transmittance. Scanning electron microscopy images revealed that the ITO rods were uniformly distributed on the ITO glass; they had large surface areas for the tethering of electrochromic molecules. As a result, the ITO nanorods functioned as optical amplifiers in the viologen-based ECDs, increasing the color contrast [ΔT (%)] from 38% to 61%.

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1. Introduction

With the explosion of green technologies, there is increasing demand for electronic devices that operate at low power. Electrochromic materials have been studied extensively in academia and industry because of their potential applications in ultralow-power-consumption devices, such as smart windows [1], anti-dazzling mirrors [2–4], electronic paper [5,6], and non-emissive electrochromic displays [7]. Electrochromism is the phenomenon of an electroactive material exhibiting a reversible, visible change in its optical absorption upon the application of an electric voltage or the passage of an electric current. Generally, electrochromic devices (ECDs) possess multilayer structures with the electrochromic materials either coated on the substrate (thin film-type) or dissolved in a sandwiched solution (chromophore-type). The former structure incorporates two films: one electrochromic film serves as a working electrode and another film (connected via an electrolyte) acts as a counter electrode. The coloration arises from intercalation of anions or cations into the thin films. Many transition metal oxides (e.g., WO_3 , MoO_3 , V_2O_5 , Nb_2O_5 , NiO) [8,9] and conjugated polymers (e.g., polyaniline, polypyrrole, polythiophene) [10–12] exhibit electrochromic behavior. In general, the polymer based materials are easier to process than inorganic electrochromic materials. The colors of the conducting polymer can also be tailored. However, there are still problems

limiting the use of polymer electrochromic materials for display devices. The operating life time of the polymers is still limited to 10^6 cycles due to the irreversibility of ionic transport and moisture [13,14]. In contrast, the electrochromic materials in chromophore-type devices diffuse or migrate to the electrode, forming a monolayer on the electrode surface, where they undergo oxidation or reduction with an associated color change. Such systems exhibit superior reversibility, relative to that of thin film-type devices, because the coloration and decoloration processes occur without ionic intercalation. Nevertheless, the electrochromic contrast in chromophore-type devices is limited by the paucity of sites for electrochromophoric molecules to undergo redox reaction. Therefore, to increase the contrast ratio of chromophore-type ECDs, it is necessary for the electrode to feature a large surface area.

There are many reports of nanostructured titanium dioxide (TiO_2) and zinc oxide (ZnO) being used as optical amplifiers that enhance the contrast ratio of chromophore-type ECDs [15–17]. This enhancement results from the large surface areas of TiO_2 and ZnO nanostructures enabling a high chromophore loading per unit area of the electrode. Unfortunately, the photocatalytic properties of TiO_2 and ZnO electrodes can lead to degradation of the anchored chromophores under illumination [18–20], thereby decreasing the stability of such ECDs. In addition, the preparation of nanocrystalline TiO_2 and ZnO must be performed using high temperature annealing, which limits the selection of the transparent conducting substrates. Moreover, in order to enhance the color contrast, the thickness of TiO_2 and ZnO should be increased to offer larger site for dye loading (usually larger than submicron scale). However, the TiO_2 and ZnO with too large thickness will

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reveal cloudy background and limit their use in certain applications. In this study, we fabricated viologen-based ECDs incorporating highly oriented indium tin oxide (ITO) nanorods as optical amplifiers. The ITO is fully non-photocatalytic due to its large band gap (3.9–4.2 eV) [21]. Therefore the chromophores will not be decomposed under illumination. The geometrical parameters of ITO nanorods were readily controlled by fine-tuning the conditions of electron beam evaporation. Viologen-based ECDs incorporating ITO nanorods as electrodes exhibited much higher contrast ratios than those of devices incorporating only plain ITO electrodes.

2. Experimental

2.1. Fabrication of ECDs

The ECDs were constructed on ITO-coated glass substrates ($< 10 \Omega \text{ sq}^{-1}$, RiTdisplay Corporation). After routine cleaning, the substrates were transferred to an electron beam evaporator for deposition of the ITO nanorods. Prior to deposition, the chamber pressure was reduced to ca. 10^{-6} Torr and the substrate temperature set at 200°C . During deposition, high-purity N_2 (flow rate: 1 sccm) was introduced into the chamber; deposition was performed at a pressure of 10^{-5} Torr. The ITO nanorods were deposited at a large incline angle (ca. 70°) with respect to the surface normal of the substrates. The deposition rate (1 nm s^{-1}) was monitored using a quartz crystal monitor. To fabricate the ECDs, an active area ($2 \times 2 \text{ cm}^2$) was created on the ITO surface using epoxy tape (3 M, USA). The taped ITO glass substrate was filled with a solution comprising 0.5 M TBABF₄, 0.01 M 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), and 0.01 M viologen in propylene carbonate. Another ITO glass substrate was applied to

form a sandwich-type device, which was sealed with Torr Seal[®] cement (Varian, MA, USA).

2.2. Characterization

Surface morphology and cross sections of the ITO nanorod were obtained using scanning electron microscopy (SEM) (Hitachi S-4700). The atomic ratio of In and Sn was determined using energy dispersive X-ray (EDX) for standardless quantification. The microstructure of ITO nanorod was observed by high-resolution transmission electron microscopy (HRTEM) using an FEI CM200 FEG transmission electron microscope at 200 kV. Cyclic voltammetry (CV) studies were performed with a three-electrode cell with 0.5 M TBABF₄ and 0.01 M viologen propylene carbonate using ITO nanorod as the working electrode, a platinum sheet as the counter electrode, and nonaqueous Ag/Ag^+ (containing 0.01 M AgNO_3 and 0.1 M TBAClO₄ in ACN) as the reference electrode. Spectroelectrochemical data were recorded on a Shimadzu model UV-1601PC spectrophotometer.

3. Results and discussions

The morphology and growth orientation of the ITO nanorods were studied using SEM. Figs. 1 and 2 display top-view and cross-sectional SEM images, respectively, of the ITO nanorods. The top-view SEM images of the ITO nanorods prepared over various deposition times reveal distinct and uniformly oriented rod profiles. The nanorod densities ranged from 5×10^9 to $2 \times 10^{10} \text{ cm}^{-2}$, depending on the deposition time. The sheet resistances of the ITO substrates presenting the ITO nanorods, measured using a four-point probe, are ranged from 9.9 to $11.9 \Omega \text{ sq}^{-1}$; i.e., almost identical to that of plate ITO

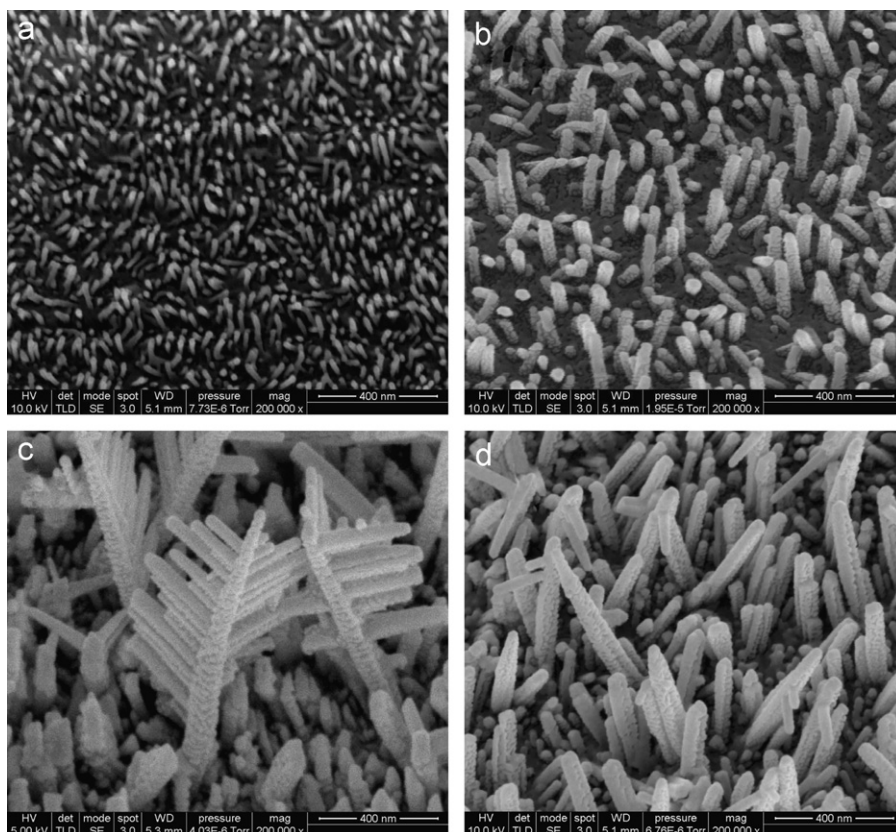


Fig. 1. Top-view SEM images of ITO nanorods deposited for (a) 200, (b) 400, (c) 800, and (d) 1600 s.

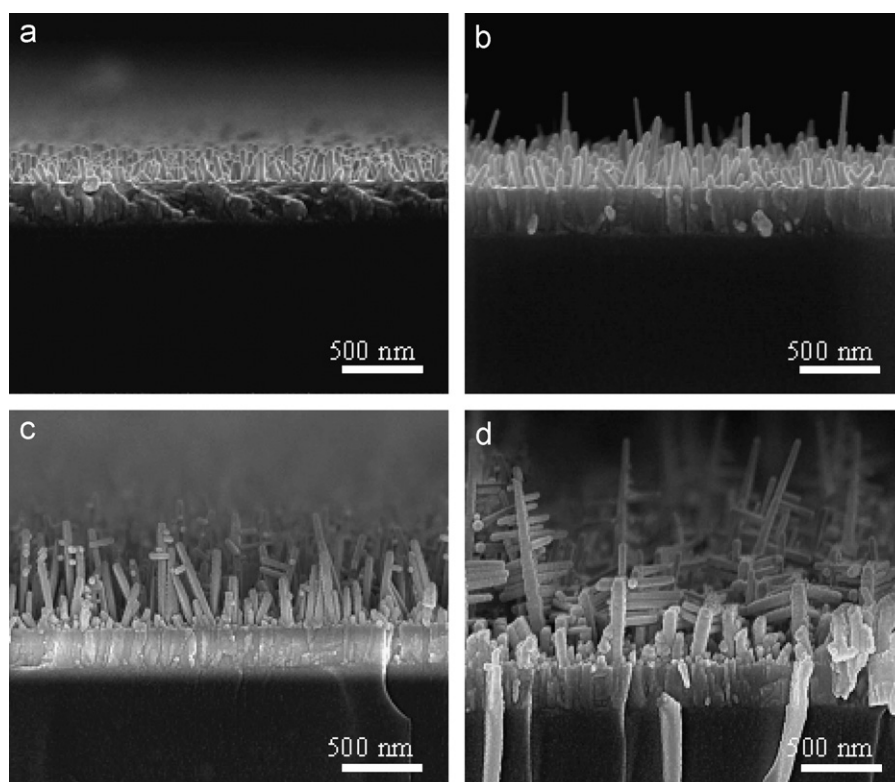


Fig. 2. Cross-sectional SEM images of ITO nanorods deposited for (a) 200, (b) 400, (c) 800, and (d) 1600 s.

Table 1

Geometrical parameters of nanorod ITO with various deposition times.

Deposited condition	200 s	400 s	800 s	1600 s
Length (nm)	100–200	200–400	400–800	650–1300
Base diameter (nm)	50	50	70	100
Top diameter (nm)	50	50	50	60
Nanorod density (cm ⁻²)	5×10^9	8×10^9	1×10^{10}	2×10^{10}

($12.4 \Omega \text{ sq}^{-1}$). The oriented morphology arose presumably from the self-shadow effect developed during grazing-angle deposition; as nuclei form, the shadowing effect quickly becomes a dominant factor in film growth [22,23]. Because a great amount of material is deposited onto the nuclei, but not into the shadowed region, rod-like morphologies are formed. Figs. 1 and 2 reveal that the nanorods deposited for 200 s had heights of 100–200 nm and diameters of ca. 50 nm; upon increasing the deposition time, these dimensions gradually increased, reaching 650–1300 nm and ca. 90 nm, respectively, after 1600 s. The details of the geometrical parameters of the ITO nanorods prepared from various deposition time are shown in Table 1. Nevertheless, many short nanorods (<100 nm) neighbored the longer ones, even after 800 s of growth, as indicated in Fig. 1e and f. These short nanorods arose from later nucleation; because the neighboring longer nanorods blocked the deposited metal flux, the short nanorods were prevented from growing. Therefore, the longer rods grew faster and longer than did the shorter ones. A high density of high-aspect-ratio nanostructures can significantly enhance the surface area of an electrode; this phenomenon has been applied in diverse fields, including dye-sensitized solar cells [24,25], gas sensors [26–28], electrochemical supercapacitors [29], and catalysis [30]. Interestingly, increasing the deposition time to 1600 s resulted in the formation of second-generation nanorods on the first-generation nanorod trunks, leading to dendritic structures.

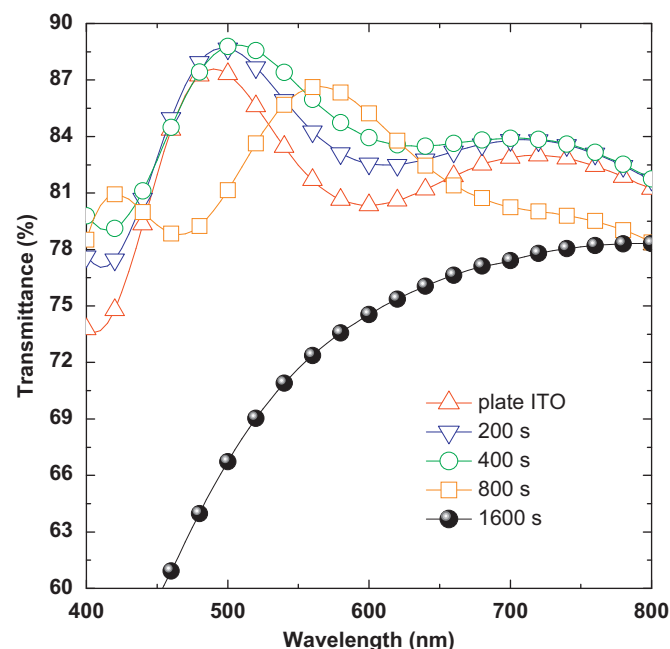


Fig. 3. Transmittances of the as-prepared ITO nanorods and the plate ITO electrode over the wavelength range from 400 to 800 nm.

Fig. S1 (Supporting Information) displays photographs of the ITO nanorod films deposited for various times. Although these structures exhibited increased surface area, their transmittance decreased dramatically, restricting their potential application in optical devices. Fig. 3 displays the transmittance spectra of the nanorods deposited for various times on the ITO films. The bare ITO film featured relatively high transmittance between 490 and 720 nm due to Fabry-Perot resonance. The nanorods deposited on

the ITO film exhibited better transmittance at certain wavelengths than that of the bare ITO film. The ITO nanorods contribute to the enhanced optical transmission is due to the reduction of the reflection at the ITO/air interface [31,32]. Notably, however, the transmittance decreased significantly for the ITO nanorods deposited for 1600 s.

Fig. 4 presents a HRTEM image and EDX spectra of the ITO nanorod deposited for 200 s. The HRTEM image reveals that the ITO nanorod possessed a core/shell structure; the EDX spectra reveal that the outer shell had a higher tin content than did the core region. When the chamber temperature is higher than the

melting point of tin-doped indium, the liquid phase nuclei have a large diffusion coefficient to enhance the absorption of indium oxide and tin oxide vapor via surface diffusion. With continuous accommodation of the oxide vapors, the liquid nuclei achieve a supersaturated state, where the nuclei are very unstable and tend to precipitate. During this stage, the precipitate appears in the core region; tin oxide is expelled from the core region to the outer shell because its melting point is higher than that of indium oxide [33]. The shell region can maintain its liquid state because of its higher tin concentration; it continues to absorb the oxide vapors. Such self-segregation results in different tin concentrations

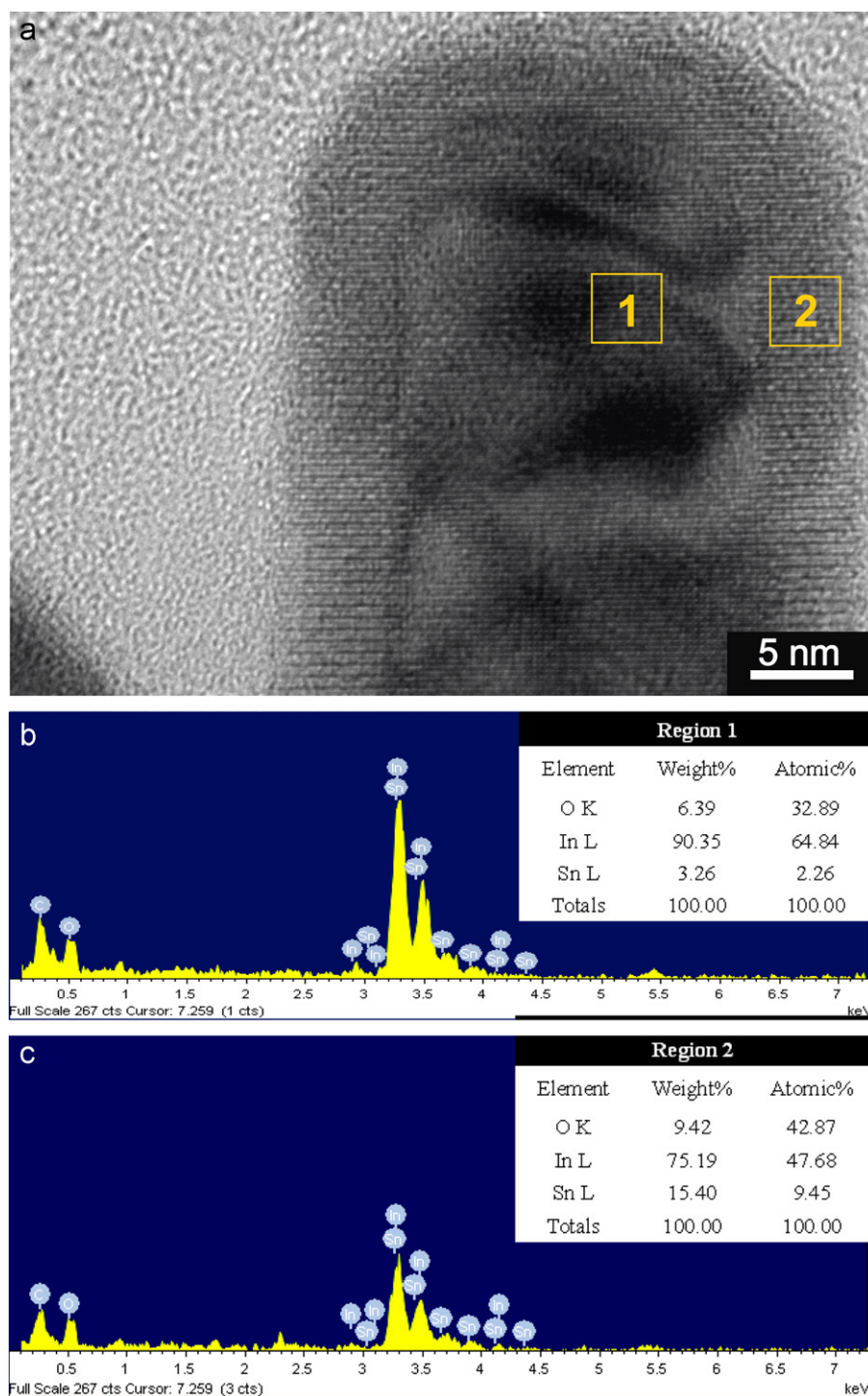


Fig. 4. HRTEM image and EDX spectra of the ITO nanorods deposited for 200 s.

between the core and shell regions. By repeating these processes, the nuclei grow to form oriented nanorods. Notably, higher conductivity can be achieved at greater tin dosages [34]; for ITO nanorods, outer shells featuring higher concentrations of doped tin exhibit better conductivity than the core region.

Fig. 5 displays the spectroelectrochemical behavior of viologen measured using the ITO nanorods of various lengths. The CV data for viologen reveal two coupled redox peaks (Fig. 5a). After reduction at -0.9 V, the color of the viologen changed to deep blue; it changed further, to pale yellow, at -1.4 V. The charge capacity of the viologen increased from 8.1 mC cm^{-2} for the bare ITO plate to 20.1 mC cm^{-2} for the ITO nanorod electrodes that had been deposited for 1600 s; the electrochemical capacitance of these ITO nanorods was 2.4 times higher than that of the flat ITO electrode. Our results suggested that longer ITO nanorods adsorbed more viologen. Fig. 5b presents in situ spectra of viologen on different ITO nanorod electrodes treated at 0 and -0.9 V. For the ITO nanorod deposited for 1600 s, the difference in absorbance (ΔA) at 605 nm between the bleached and colored states was 0.7, much greater than that of the flat ITO electrode (0.34). The enhanced electrochromic contrast (EC) arose from the nanostructure of the electrode, which acted as an optical amplifier. The EC ΔA of the ITO electrodes can be expressed [35–37] as

$$\Delta A = \Gamma_v \varepsilon_v 1000 \quad (1)$$

where Γ_v is the surface concentration of viologen on the electrode, ε_v is the extinction coefficient of the viologen radical in

solution ($14,000 \text{ M}^{-1} \text{ cm}^{-1}$), and the coefficient 1000 is the dimension correction factor. Using the equation, we estimated the surface concentrations of viologen on the flat and ITO nanorod electrodes (1600 s) to be 2.4×10^{-8} and $5.0 \times 10^{-8} \text{ mol cm}^{-2}$, respectively; thus, the surface concentration on the ITO nanorod was 2.1 times higher than that on the flat ITO electrode. This surface concentration ratio is roughly consistent with the charge capacity ratio. Fig. 5c displays the ECD transmittance responses for darkening and bleaching for the bare plate and ITO nanorod electrodes; Table 2 summarizes the data. When we set the darkening and bleaching voltages at 1 and 0 V, respectively, we observed a reversible transmittance changes of greater than 55% for the ITO nanorod electrodes that had been deposited for 800 and 1600 s. Fig. 5d presents optical images, under bleaching and

Table 2

Performance Data for ECDs Fabricated Using Different ITO Nanorod Electrodes.

Electrode	Transmittance change ^a			Response time at 0.9 ΔT	
	T_{darken} (%)	T_{bleached} (%)	ΔT (%)	τ_{darken} (s)	τ_{bleached} (s)
Plate ITO	37.7	75.8	38.1	4.6	3.8
200 s	33.3	77.1	43.9	4.0	3.7
400 s	25.8	77.0	51.3	4.4	3.8
800 s	18.0	78.0	60.0	4.8	4.0
1600 s	6.0	67.5	61.4	4.3	4.0

^a The transmittance change was recorded at 605 nm.

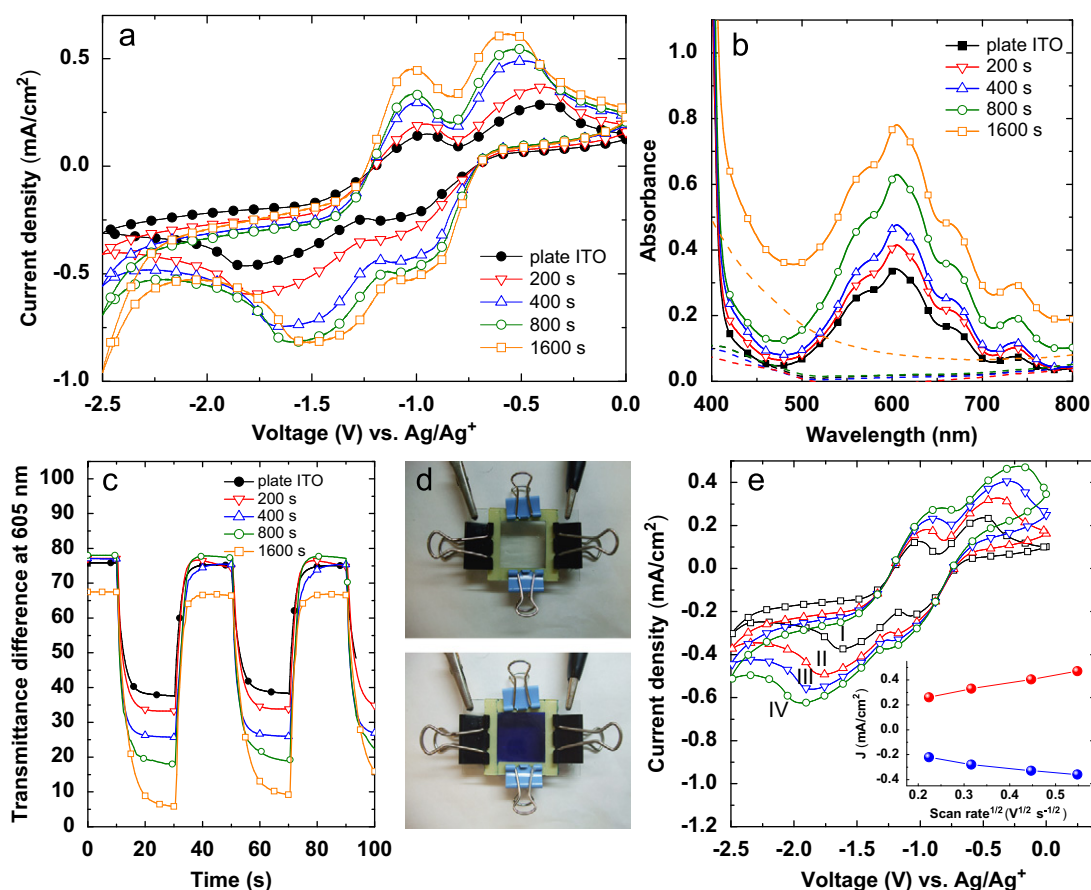


Fig. 5. (a) CV traces for 0.01 M viologen in propylene carbonate supplemented with 0.1 M TBABF₄, measured using ITO nanorod electrodes prepared for different deposition times. (b) In situ spectra of viologen at 0 and 0.9 V on ITO nanorod electrodes. (c) Transmittance time responses for viologen/TEMPO ECDs upon applying a darkening voltage of 0.8 V and a bleaching voltage of 0 V, using ITO nanorods as electrodes. (d) Digital photographs of the ECD incorporating ITO nanorods deposited for 1600 s as electrodes, in its bleached and darkened states. (e) CV traces of viologen recorded at potential scan rates of (I) 50, (II) 100, (III) 200, and (IV) 300 mV s⁻¹. Inset: Peak current plotted as a function of the square root of the scan rate. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

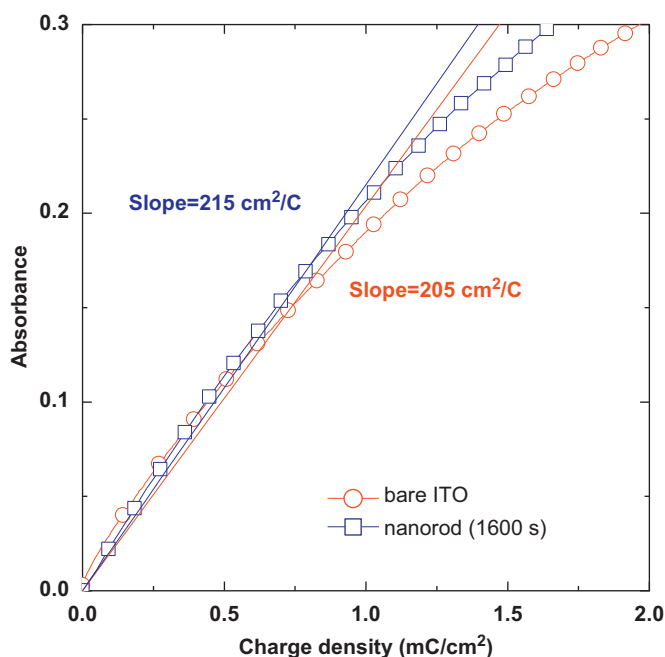


Fig. 6. The coloration efficiency of the viologen measured using the flat ITO and nanorod electrodes.

darkening states, of the ECD incorporating the ITO nanorod electrode that had been deposited for 800 s. Although the ITO nanorods deposited for 1600 s provided the highest transmittance change (61%) among these electrodes, the intrinsic low transmittance of these ITO nanorods (Fig. 3) reduced the ECD's transmittance in the bleaching state and limited their applicability. Table 2 reveals that the response times (τ) of the ECDs, for both darkening and bleaching, were almost identical. This phenomenon can be explained by considering the reaction mechanism. Fig. 5e displays the variation of the current density (i_p) of viologen with respect to the scan rate (v , up to 400 mV s^{-1}). We observe a linear relationship between i_p and $v^{0.5}$, indicating that the redox reaction is a diffusion-controlled process. Under the same applied voltage and electrolyte, the diffusion coefficient of viologen should be a constant. Therefore, the response times of the ECDs were roughly the same and independent of the nature of the electrode.

The coloration efficiency of the EC device can be defined by $C(\lambda) = \Delta A(\lambda) / \Delta Q$, where ΔQ is the corresponding accumulated charge for absorbance change, $\Delta A(\lambda)$. Therefore, the coloration efficiency can be determined from the slope of the plot of the absorbance A versus the accumulated charge Q . The input charge density versus absorbance is shown in Fig. 6. The coloration efficiency of viologen measured using plate ITO and ITO nanorod can be extracted from the slope in Fig. 6. A linear relationship between the absorbance and the accumulated charge is found initially. The calculated coloration efficiency of viologen measured using the ITO nanorod was ca. 215 C cm^{-2} ; it was very close to that (205 C cm^{-2}) measured using the flat ITO electrode. A similar coloration efficiency means that the resistance between the electrodes and electrolyte remained almost identical for both systems.

4. Conclusion

In summary, we have used oblique electron beam evaporation in a nitrogen-rich environment to prepare distinctive ITO nanorod electrodes. The ITO nanorod electrodes exhibited high transmittance over a broad range of wavelengths and high aspect ratios.

ECDs incorporating the nanostructured ITO electrodes exhibited similar color switching speeds and color efficiencies as those of the ECD incorporating a flat ITO electrode, but with better performance in terms of color contrast because of the higher surface areas of the nanostructures.

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Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.solmat.2011.10.027.

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