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Enhanced optical and electrical properties of PEDOT via nanostructured carbon materials: A comparative investigation

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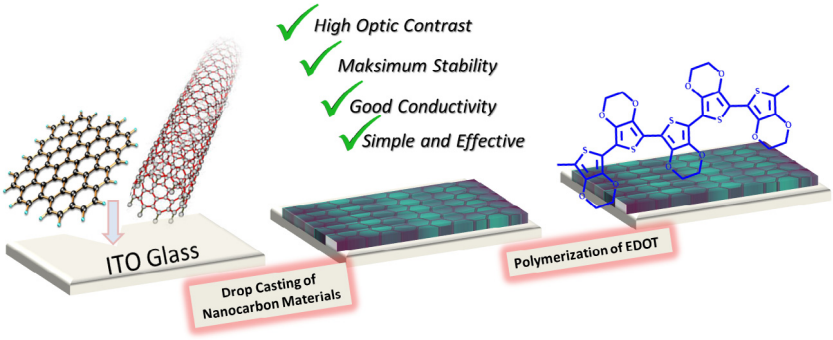
GRAPHICAL ABSTRACT



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ABSTRACT

Addressed herein, novel poly(3,4 ethylenedioxythiophene) PEDOT/Nanocarbon Materials (NCMs) composite films have been produced by electropolymerization of EDOT monomers onto NCMs coated indium tin oxide (ITO) glass slides. In this study NCMs/ITO working electrodes were prepared by drop casting method which is simpler, quicker, cheaper and easier than other methods. Then PEDOT/NCMs composite films have been produced and investigated by comparing the electrochemical properties with each other in this study. These novel materials significantly improved conductivity and electrochemical performance of PEDOT such as stability of electrochromic characteristics, coloration efficiency, switching time due to an important role in the electron transfer between NCMs and PEDOT films. The prepared novel PEDOT/NCMs composites exhibit excellent optical contrast that is 2 times higher than that of others. These nanocomposite films can be used for electrochromic and energy storage devices applications in near future.

1. Introduction

NCMs have received considerable attention recently due to their specific properties like high electronic mobility and heat conductivity [1,2]. NCMs play important roles in various fields such as electronic devices [3], sensors [4,5], optics [6] and storage of energy [7,8]. As significant polymer/NCMs composites, they aroused great interest by the researchers studying advanced materials as a new class. Conductive polymers of (CPs)/NCMs composites have been investigated as transparent conducting electrode materials that complement ITO due to their excellent electrochemical, capacitance properties and physicochemical stabilities [9–11]. Various

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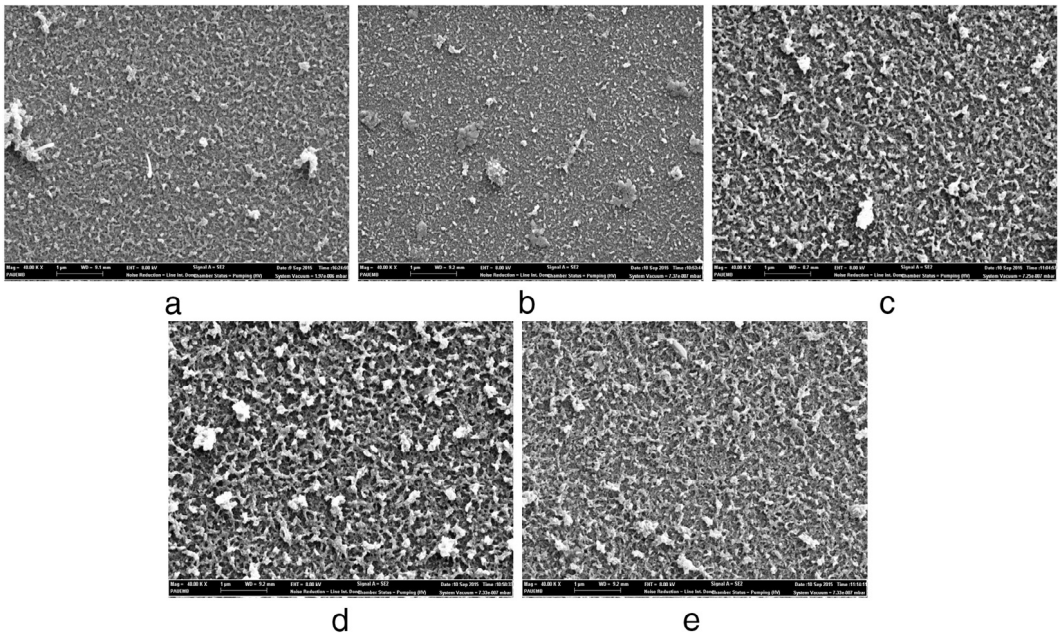

Fig. 1. SEM images of (a) PEDOT (b) PEDOT/GO (c) PEDOT/rGO (d) PEDOT/MWCNT (e) PEDOT/fMWCNT films on ITO at 40.0 K × magnification.

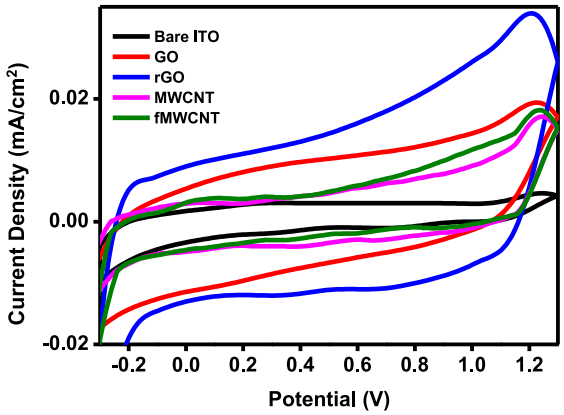

Fig. 2. CVs for NCMs-coated ITO at a scan rate of 50 mV/s in 0.1 M $LiClO_4$/ ACN without monomer.

techniques such as spraying [12], dipcoating [13], spin-coating [14] have been studied for the preparation of transparent and conductive composite films so far.

Electrochromic materials show a reversible optical change in absorption upon being electrochemically oxidized or reduced at which they have been implemented as smart windows [15–17]. As an organic electrochromic material, the 3,4 ethylenedioxythiophene (EDOT) has been used widely due to switching the color fast from deep-blue to pale-blue hues. It has also large electronic conductivity, high transmissivity and low band gap [18].

The aim of this study is to prepare PEDOT/NCMs composite films and investigate electrochromic properties of these films comparatively. Few literatures are focused on NCMs with conducting polymers like aniline, pyrrole or EDOT, but those polymers were mixed with the nanocarbon material before the preparation of the composites [19–21]. However, in this study NCMs/ITO working electrodes were prepared by drop casting method which is more simple, quicker, cheaper and easier than other methods. Then PEDOT/NCMs composite films have been produced and investigated by comparing the electrochemical properties with each other in this study. Four different NCMs compounds are prepared by being dispersed and coated onto ITO by Graphene Oxide (GO), reduced Graphene Oxide (rGO), Multiwalled Carbon Nanotube (MWCNT) and functionalized MWCNT (fMWCNT) under the same conditions. PEDOT was electrodeposited on NCMs coated ITO and we hope that $\pi-\pi$ interactions, transport and adsorption of electrolyte ions on PEDOT/NCMs composite films will improve performances of optical and electrical features. A comparison between PEDOT/NCMs films and PEDOT/ITO control film in terms of electrochemical activity, stability, coloration efficiency, and switching kinetics was achieved successfully.

2. Experimental section

2.1. Synthesis of nanostructured carbon materials

Graphene oxide (GO) was synthesized by graphite powder through a modified Hummers method [22,23]. Reduced graphene oxide (rGO) has been prepared in the presence of hydrazine hydrate that was added into the GO solution [24,25]. The functionalization of multiwalled carbon nanotubes (f-MWCNT) has also been performed by acid treatment. Synthesis and characterization of NCMs are given in supporting information.

2.2. Preparation of NCMs dispersions

ITO glasses were coated with NCMs by drop-casting technique. In this study, the most requested feature is that ITO glass surface becomes homogeneous and transparent after coating with NCMs. Film thickness depends on the solution concentration. In order to control film uniformity, the substrate is heated to speed up the evaporation process. For this study, firstly, 0.5 mg NCMs was added to 3 μl DMF in an agitate in mortar and thoroughly hand-mixed (water was used for MWCNT). DMF was added to obtain the total volume of 25 ml for dispersion and then ultrasonicated for 30 min. ITOs were carefully cleaned by a detergent solution, ultrasonicated for 10 min and washed with distilled water and ethanol, respectively [26]. A part of the ITO plates was covered with Teflon band to create 1.2 cm^2 (0.6 cm × 2 cm) working area. 50.00 μl of each dispersions was dropped onto the working area using a micropipette at 80 °C without touching the surface of the ITO plates.

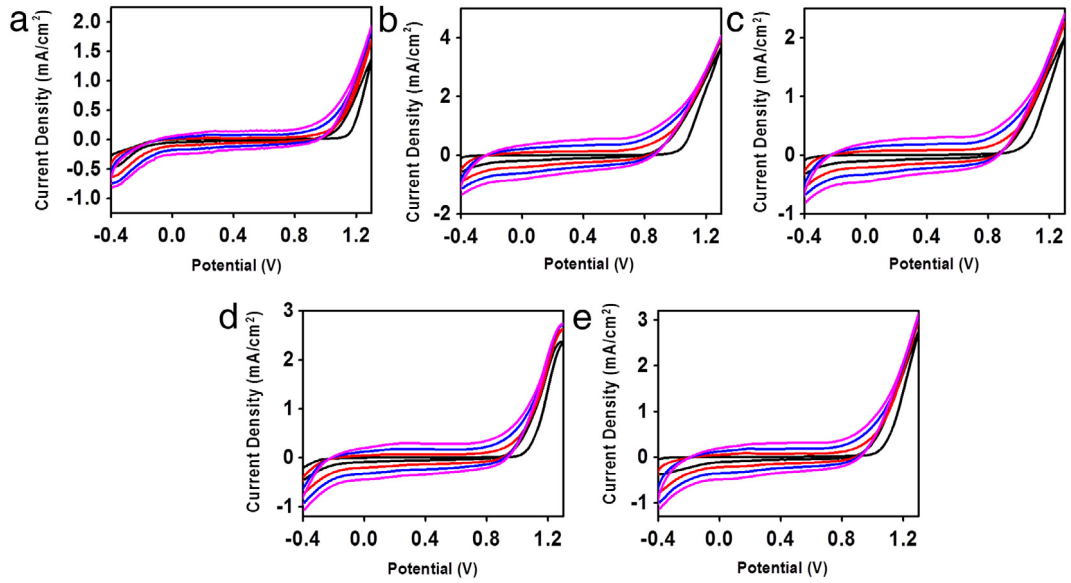

Fig. 3. Cyclic voltammogram of electrodeposition of EDOT on (a) bare ITO (b) GO (c) rGO (d) MWCNT (e) fMWCNT coated electrodes in 0.1 M $LiClO_4$/ACN electrolyte–solvent couple.

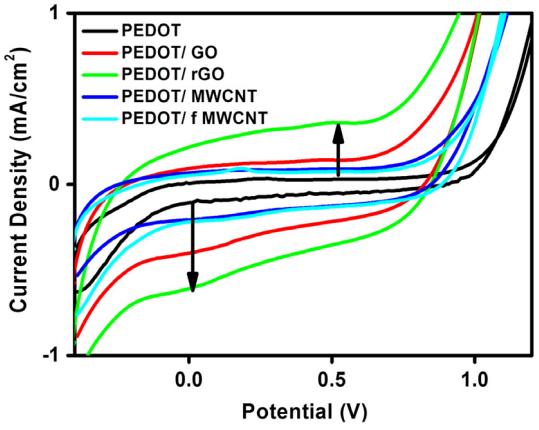

Fig. 4. The comparison of second cycle of PEDOT/NCMs composite films.

2.3. Preparation of PEDOT/ NCMs composite films

The working electrode (NCMs–ITO) was prepared according to the procedure described above. Platinum wire was used as counter electrode whereas silver wire was used as the pseudo-reference electrode for electrodeposition of EDOT from NCMs–ITO films in three-electrode cell. The oxidation–reduction behaviors of EDOT/NCMs were examined by cyclic voltammetry (CV). Electrochemical polymerization of EDOT (0.037 M) was performed by CV in 0.1 M $LiClO_4$/ACN.

2.4. Investigation of spectroelectrochemical properties

Spectroelectrochemical analyzes were carried out to understand the band structure of composites. For spectroelectrochemical analyzes and the preparation of polymer films, 0.037 M EDOT dissolved in 0.1 M $LiClO_4$/ACN was deposited between −0.3 V and 1.4 V for 4 cycles on NCMs coated ITO. UV spectrum of the PEDOT/NCMs films were studied at different applied potentials in monomer free 0.1 M $LiClO_4$/ACN electrolyte/solvent couple system.

Optical spectroscopy was coupled with square wave potential step which was utilized to investigate the switching times and optical contrast for PEDOT/NCMs films. In square wave potential step experiment, the potential was adjusted as the initial potential for 5 s and stepped to a second potential for another 5 s. Transmittance percentage (%T) and switching times at maximum wavelengths of the composite films were obtained by UV–Vis spectrophotometer.

3. Results and discussion

3.1. Surface characterization of NCMs composite films

SEM images of all materials coated on ITO glass are obtained for surface morphology investigation. Fig. 1 demonstrates FESEM images of PEDOT and PEDOT/NCMs electrodes. According to all these images obtained, it can be concluded that the NCMs are well covered on ITO surface. Furthermore, after polymerization of EDOT, the resulting PEDOT/NCMs composite films have uneven surface with some clusters gathered on the surface and show highly porous morphology. This porous network structure provides the electron transportation and improves conductivity, electrochemical properties of the PEDOT/NCMs composite films. Also in PEDOT/MWCNT and PEDOT/fMWCNT composite films, PEDOT could be enwrapped the carbon nanotube by the distinctive interconnected nanotubular structure.

The NCMs coated ITOs and bare ITO were both cycled between −0.4 V and 1.3 V at a scan rate of 50 mV/s in monomer free solution. Fig. 2 shows the comparative CV plots of NCMs and bare ITO. Before electropolymerization of EDOT, capacity of current density of NCM-coated ITO surfaces was investigated. Current rise was observed in the NCM-coated ITO surfaces as shown in integrated CV area. The highest current rise was detected for rGO because of capability of deposition charge on ITO electrodes.

3.2. Cyclic voltammogram of PEDOT/NCMs composite films

The system is comprised of a potentiostat and a CV cell with different NCMs coated ITO glass slide 1.2 cm^2 (0.6 cm × 2 cm) as working electrode. In order to make comparison, firstly EDOT (0.037 M) was deposited potentiodynamically between −0.4 V and 1.3 V at a scan rate of 50 mV/s in 0.1 M $LiClO_4$/ACN. Then, under the same conditions EDOT (0.037 M) was deposited on the NCMs coated ITO electrodes (Fig. 3). There is an increase in the intensity of the current as the number of cycles for PEDOT and PEDOT/NCMs. After first scan the appearance of reversible redox couples and an

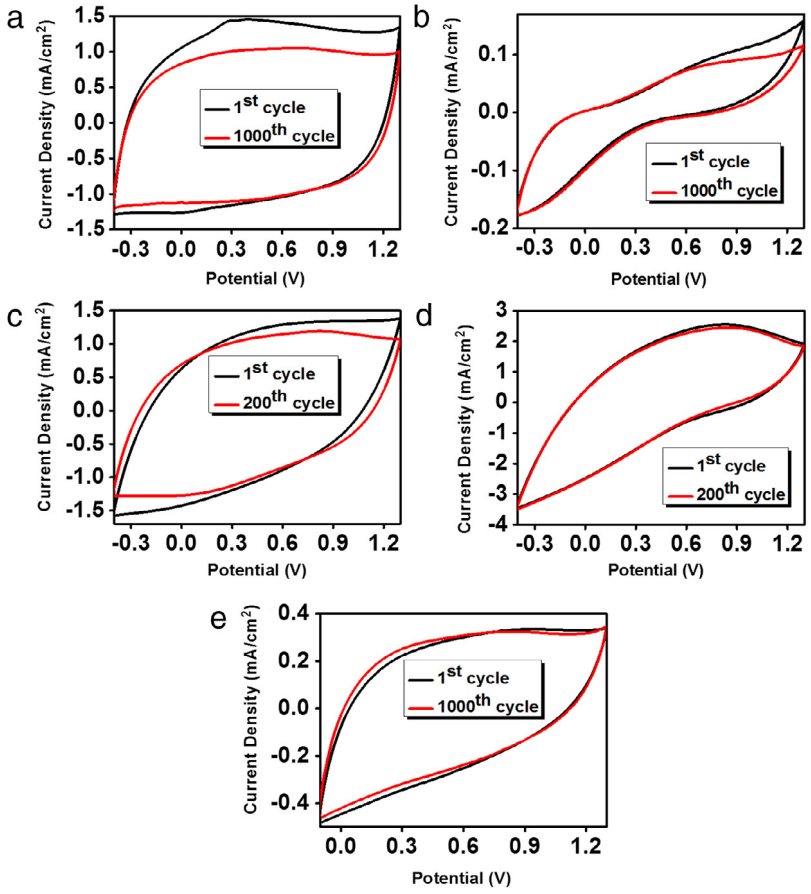

Fig. 5. Stability graphs of (a) PEDOT (b) PEDOT/GO (c) PEDOT/rGO (d) PEDOT/MWCNT (e) PEDOT/fMWCNT in 0.1 M $LiClO_4$/ACN electrolyte–solvent couple.

increase in the redox couple currents demonstrate the formation of a PEDOT on the NCMs coated ITO surfaces. Besides, Fig. 4 shows the comparison of second cycle of PEDOT/ NCMs composite films in CV. It was observed that the current rises of PEDOT/NCMs composite films are higher than that of bare EDOT when all conditions are kept constant. This large size of integrated CV areas depend on the amount of charge loaded on the ITO electrodes. As is also shown in Fig. 2, charge density of rGO coated ITO electrode has the largest CV area among the other NCM coated ITO electrodes. The charge holding capacity of PEDOT/rGO is higher compared to others indicating that high rate of electrochemical process refers to the fast diffusion of counterion and electron.

3.3. Stability of PEDOT/NCMs composite films

Redox stability is a significant necessity for the production of reliable electrochromic devices having long life time. CV techniques are important methods used to investigate the long-term stability. Electrochemical stability determine from degradation of the active center between first cycle and 1000th cycle. This charge density was calculated from integration of CV of PEDOT/NCMs films between first cycles and 1000th cycles. For this purpose, we obtained the PEDOT/ NCMs composites by non-stop cycling process between −0.4 V and 1.3 V at scan rate of 500 mV/s in monomer free solution.

As seen in Fig. 5, even after 1000th run, PEDOT/NCMs composite films retained high majority of all of its electroactivity, representing the electrochemical stability of continuous switching. The stability of PEDOT/ITO, PEDOT/GO–ITO, PEDOT/rGO–ITO, PEDOT/MWCNT, PEDOT/fMWCNT composite films between first and last cycles was 85.11%, 98.40%, 95.36%, 96.65%, 99.92%, respectively. Stability of all PEDOT/NCMs composite films is higher than that of PEDOT film. However PEDOT/fMWCNT composite film shows the best stability after 1000 cycles. The reason for improvement in stability is that the π-π^* interaction between the carboxyl groups of the fMWCNT and the quinoid rings of PEDOT increased the degree of electron delocalization between the components, effectively. In these nanocomposite systems, the PEDOT is a good electron donor, whereas fMWCNT is considered to be an acceptor. Therefore, the fMWCNT ensure dopant effect or facilitate charge transfer from the quinoid units of PEDOT to the fMWCNT leading to increase in stability of the composite.

3.4. Spectroelectrochemical properties of PEDOT/NCMs composite films

Spectroelectrochemistry is used for examining the changes in optical properties upon doping and provides information about the electronic structure of Cp such as intraband states and band gap (Eg). PEDOT films were electrochemically synthesized by NCMs–ITO electrode in 0.1 M $LiClO_4$/ACN electrolyte–solvent couple. Spectroelectrochemical measurements of the PEDOT/NCMs composite films were performed by applying potentials between −1.5 V and 1.5 V in monomer free solution. Fig. 6 stands for the UV–Vis spectrum of PEDOT/NCMs composite films studied at different applied potentials. Maximum wavelength of π–π^* transitions was observed at 600 nm for all studies. Band gap and transmittance percentage ($\%\Delta T$) were obtained as 1.55 eV and 24% for PEDOT/, 1.40 eV and 33% for PEDOT/GO, 1.40 eV and 47% for PEDOT/rGO, 1.42 eV and 33% for PEDOT/MWCNT, 1.54 eV and 34% for PEDOT/fMWCNT, respectively. The band gap values of the composite films were smaller than those of the PEDOT's band gap. Low band gap values provide the electron modulation between NCMs

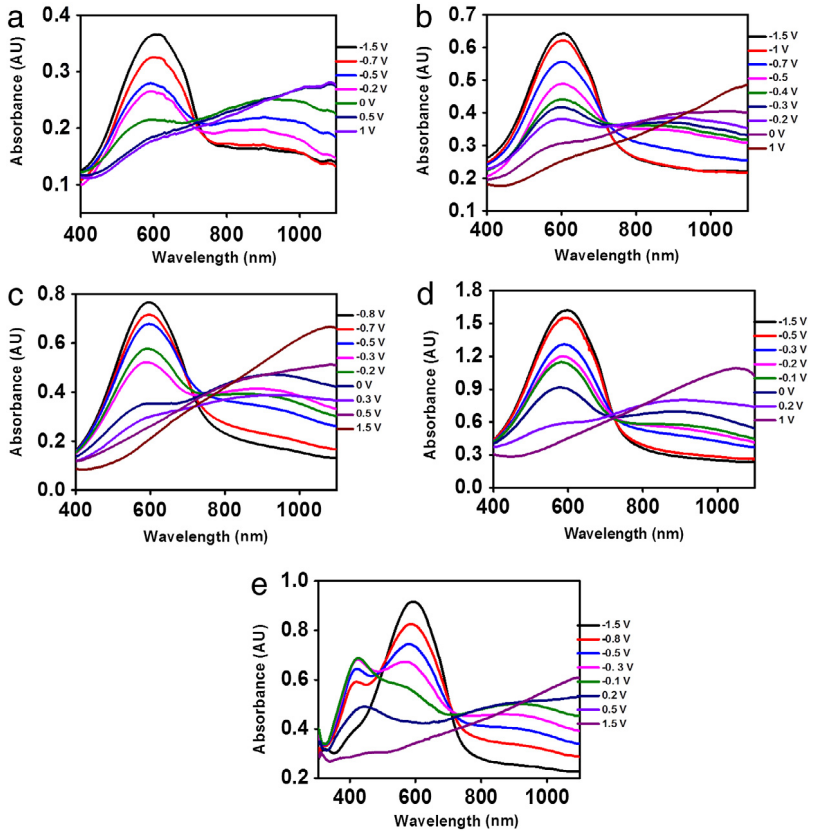

Fig. 6. Spectroelectrochemical spectrum of (a) PEDOT (b) PEDOT/GO (c) PEDOT/rGO (d) PEDOT/MWCNT (e) PEDOT/fMWCNT in 0.1M $LiClO_4$/ACN electrolyte–solvent couple.

and PEDOT at the interband. The percentage of transmittance of PEDOT/NCMs composite films considerably higher than that of bare PEDOT film. PEDOT/rGO composite reached the highest optic contrast (47%) between transmissive neutral state and the colored oxidized state. rGO–ITO shows the highest current value as the working electrode. Hence, PEDOT electrodeposition PEDOT/rGO composite film represents excellent oxidation–reduction behavior as well as the good ion transport agent between PEDOT and rGO–ITO surface. The highest absorbance value was observed for PEDOT/MWCNT and the color of PEDOT/MWCNT composite film was dark blue due to unique black solution of MWCNT. PEDOT can be enwrapped to MWCNT structure as easier than other composite films. Transmittance yield of PEDOT/MWCNT composite film was 33%. As a result of the optical contrast enhancement, according to Fig. 7, PEDOT film on ITO depicts blue color, whereas, PEDOT/NCMs composite films depict darker blue color in neutral state under the same conditions. All of these diversities indicate that NCMs play a significant role in the high optical contrast, redox response and tuning band gap for electrochromic applications.

Color switching capabilities of PEDOT/NCMs composite films were obtained by the highest and lowest transmittance values in kinetic plots. EDOT was electrodeposited on NCMs coated ITO film to investigate electrochromic switching studies via CV technique between −0.3 V and 1.4 V. The response time of the PEDOT/NCMs composites was calculated by the transmittance percentage (%T) at 600 nm through switching the applied potential in redox states between −1 V and 1.5 V square wave potentials with 5 s time intervals. As shown in Fig. 8, switching time of PEDOT, PEDOT/GO, PEDOT/rGO, PEDOT/MWCNT, PEDOT/fMWCNT composite films are 2.9 s, 1.5 s, 3.1 s, 2.3 s, 2.2 s at 600 nm, respectively. Switching time of conducting polymer depends on ion transportation during oxidation step of the redox process. Especially for high switching rates, ions must reach to the holes on the oxidizing polymer. GO

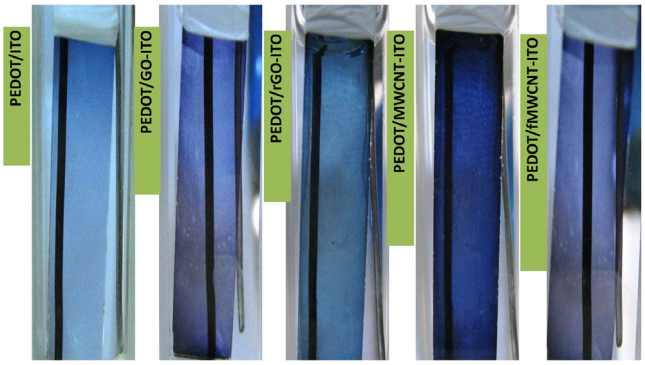

Fig. 7. Photo of PEDOT/NCMs composite films in neutral state under the same conditions. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

structure is more suitable for electron injection due to acidic functional groups. Therefore, switching time of PEDOT/GO composite film was faster than that of PEDOT/rGO composite film.

Coloration efficiency (CE) which is described as optical density (OD) was induced by unit charge density (Qd) which is used for a state between the bleached state and the colored state of PEDOT film and applied for obtaining amount of energy to affect a color change. CE can be determined by utilizing the following equation [27].

$$CE = \Delta OD/Qd$$

$$\Delta OD = \log[T\text{colored}/T\text{bleached}]$$

Qd ($mC\ cm^{-2}$) was calculated by charge–time plots and CE value of PEDOT, PEDOT/GO, PEDOT/rGO, PEDOT/MWCNT, PEDOT/fMWCNT

Table 1
Stability, switching time, Eg and CE values of PEDOT and PEDOT/NCMs composite films.

	PEDOT/ITO	PEDOT/GO	PEDOT/rGO	PEDOT/MWCNT	PEDOT/fMWCNT
Stability %	85.11	98.4	95.36	96.65	99.92
Eg (eV)	1.55	1.4	1.4	1.42	1.54
Switching time (s)	2.9	1.5	3.1	2.3	2
ΔOD	0.19	0.39	0.57	1.15	0.58
T%	24	33	47	33	34
Qd (mC cm^{-2})	8.06	5.812	8.63	13.01	12.02
CE (cm^2 C^{-1})	23.57	67.1	66.04	88.3	48.2

Table 2
Summarized a comparison of spectroelectrochemical properties of PEDOT/NCMs composite films in the literature.

Material	λ_{max} (nm)	Switching time (s)	Optical contrast (%)	Reference
PEDOT–MWCNT	632 nm	2.8	23	[21]
PEDOT–RGO	632.8	3	27	[19]
PEDOTF	600	2	38.94	[28]
PEDOT–IFGR	485 nm	2.3	25	[29]

PEDOTF: Polymerization of EDOT-modified functional-MWCNT.
PEDOT–IFGR: Polymerization of EDOT with ionic liquid functionalized graphene.

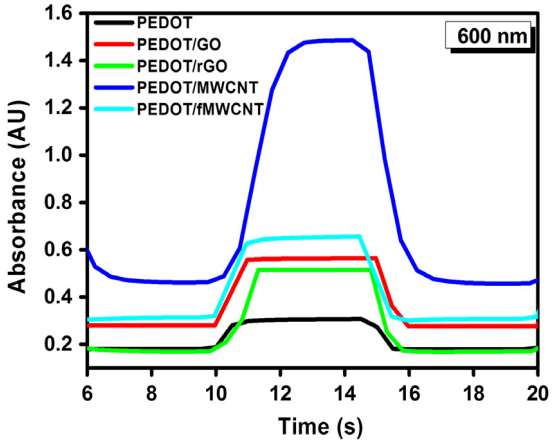

Fig. 8. Single step of electrochromic switching for PEDOT and PEDOT/NCMs composite films between −1.5 V and +1.5 V.

film was found as 23.57 cm^2 C^{-1}, 67 cm^2 C^{-1}, 66 cm^2 C^{-1}, 88 cm^2 C^{-1}, 48 cm^2 C^{-1} at 600 nm, respectively. PEDOT/MWCNT film was reached to maximum CE value and that is 3.5 times greater than that of PEDOT film. The better porosity provided by the nanotubular structure of the PEDOT/MWCNT composite film enables charge injection and thus it showed stable color-bleach kinetics. The electrodes of these composite films can be used for electrochromic devices having longer lifetime because of strong electrical interaction between NCMs and PEDOT. Table 1 and Table 2 provide a comparison of the stability, switching time, Eg and CE values for the PEDOT and PEDOT/NCMs composite films.

4. Conclusions

The PEDOT/NCMs composite films have been prepared by electrodeposition of PEDOT onto the NCMs coated ITO glass as novel materials. We have investigated the electrochemical and spectroelectrochemical performance of ITO with and without NCMs, and found higher values than that of the PEDOT in terms of current density, stability, optical contrast, coloration efficiency. The prepared novel materials demonstrate excellent stability when compared with PEDOT film. Besides, PEDOT/rGO composite film exhibited excellent optical contrast that is 2 times higher than that of the PEDOT film. Furthermore, PEDOT/MWCNT composite film showed very high CE value (88.3 cm^2 C^{-1}). The band gap values of PEDOT/NCMs composite films were calculated in the range of 1.40–1.55 which was highly smaller than that of PEDOT. The PEDOT/NCMs composite films demonstrated more enhanced features than that of the PEDOT films in the redox behaviors and optical contrast due to the excellent interactions between the polymer and the GO, rGO. Also PEDOT/MWCNT composite films showed good stability and high CE values depending on nanotubular, porous structures of MWCNT. As a conclusion, the novel PEDOT/NCMs composite films will show highly promising potentials for the electrochromic, solar cell and energy storage devices applications in near future because of extraordinary properties such as excellent stability, current density, optical contrast, CE.

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Appendix A. Supplementary data

Supplementary material related to this article can be found online at http://dx.doi.org/10.1016/j.nanoso.2017.05.008.

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