

# Development of Electrochromic Device Based on Electrodeposition and Chemical Bath Deposition for Nickel Oxide Thin Films Doped with Efficient Multichromatic Polymers

A.A.Kulkarni

*Department of Physics, D.Y.Patil College of Eng. & Tech., Kolhapur, India*

S.S. Tupe

*Department of Physics, D.Y.Patil College of Eng. & Tech., Kolhapur, India*

A.V. Kadam

*Department of Physics, D.Y.Patil College of Eng. & Tech., Kolhapur, India*

**Abstract - Nickel oxide/Polypyrrole (NiO/PPy) thin films were deposited by a two step process in which the NiO layer was electrodeposited potentiostatically from an aqueous solution of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  at pH 7.5 on fluorine doped tin oxide (FTO) coated glass substrates, followed by the deposition of polypyrrole (PPy) thin films by chemical bath deposition (CBD) from pyrrole mixed with ammonium persulfate (APS). Similarly Nickel oxide thin films were electrodeposited from an aqueous solution of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  at pH 7.5 on fluorine doped tin oxide (FTO) coated glass substrates and a layer of polyaniline (PANI) was formed on NiO thin films by chemical bath deposition (CBD). The NiO/PPy and NiO/PANI films were further characterized for their electrochromic properties. The electrochromic (EC) property of the film was studied using cyclic voltammogram (CV), chronoamperometry (CA) and optical modulation. The NiO/PPy presents superior EC properties than their individual counterparts. NiO/PANI films shows electrochromism with color changes from pale yellow to dark green - purple in the reduced states to dark blue -dark green-light green (photomeraldine at -0.7 V vs SCE) in its oxidized states. The colouration/bleaching kinetics of NiO/PPY (response time of few ms) and colouration efficiency ( $358 \text{ cm}^2/\text{C}$ ) were found to be improved appreciably whereas CE of NiO/PANI film was  $85 \text{ cm}^2/\text{C}$  with response time for reduction and oxidation were found to be 20 and 60 ms respectively. This work therefore demonstrates a cost-effective and simple way of depositing highly efficient, faster and stable NiO/PPy, NiO/PANI electrodes for EC devices.**

**Key words: Nickel Oxide thin films, Polypyrrole (PPy), Polyaniline (PANI), Electrodeposition, Chemical Bath Deposition (CBD), EC Properties.**

## I. INTRODUCTION

Nanoporous network provides specific surface area and can facilitate the contact between electrolyte and oxide surface with open space between individual pores which allows the easier diffusion of ions among them. Organic-inorganic electrochromic device would deploy a material with high colouration efficiency, faster response time and outstanding operation life time. Organic-inorganic hybrid materials represent a new class of materials as they can combine the advantages of both the components and offer special properties through modification of each other [1].

In this paper NiO/PPy and NiO/PANI samples have been prepared by using simple electrodeposition and CBD techniques. Electrodeposition is of particular interest due to low-cost, environmental friendly process, and feasibility of room temperature growth on large area for the deposition of NiO films. On the other hand, the advantage of chemical synthesis is that it offers mass production at a reasonable cost for polypyrrole films, without compromising on quality. The EC performance of NiO/PPy and NiO/PANI film were tested in  $\text{LiClO}_4\text{-PC}$ . CA was used to determine the response time of the colouration-bleaching process of the device. The electrochemical stability was examined, by repeating colour/bleach cycles in an electrolyte for prolonged period.

The NiO/PPy and NiO/PANI presents superior EC properties than their individual counterparts. The colouration/bleaching kinetics, colouration efficiency and electrochemical stability were found to be improved appreciably. This work therefore demonstrates a cost-effective and simple way of depositing highly efficient, faster and stable NiO/PPy and NiO/PANI electrodes for EC devices.

II. EXPERIMENTAL

NiO/PPy and NiO/PANI films were prepared sequentially by adopting electrodeposition and CBD techniques. In the first part nickel oxide thin films were electrodeposited from an aqueous nickel chloride bath containing 0.5 M nickel chloride (LOBA CHEMIE Extra Pure 97%) and 0.1M KCl onto FTO (15-20 Ω/□) coated conducting glass substrates. The three electrode electrochemical cell was used to deposit NiO thin films in potentiostatic mode in which graphite was counter electrode, SCE was reference electrode.

In the second part, polypyrrole (PPy) was synthesized using monomer Pyrrole (0.03M in 100 ml distilled water) chemically polymerized with ammonium persulphate [(NH4)2S2O8] APS 0.06 M in 50 ml distilled water). Simultaneously polyaniline was prepared at room temperature using a chemical bath consisting of ammonium persulphate, hydrochloric acid, aniline and distilled water. NiO film was dipped into the solution for 10 s and dried in air for 30 minutes. This dipping and drying process was repeated twice so as to produce desired thickness of film. Thus NiO/PPy and NiO/PANI film were prepared for electrochromic application and electrochromism was tested with a standard three electrochemical cell of configuration,

Glass/FTO/NiO/PPy/1M LiClO4 + PC/ SCE Glass/FTO/NiO/PANI/0.1M LiClO4 + PC/ SCE

The CV measurements were carried out in the potential range -1.5 to +1.5 V (vs SCE) with a scanning rate of 20mV/s for NiO/PPy whereas CV measurements were carried out in the potential range -1.5–2.2 V (vs SCE) with a scanning rate of 50mV/s for NiO/PANI at room temperature. Optical absorption and transmittance spectra of the samples in the coloured and bleached states were recorded using UV-Vis-NIR spectrophotometer, (Systronics-model 119) over 350-1000 nm.

III. RESULTS AND DISCUSSION

3.1 Electrochromic and electrochemical properties

Fig. 1 (a-c) shows the CVs recorded for NiO, PPy and NiO/PPy films in 1M LiClO4 + 1mM PC solution at 20mV/s. A simplified reduction scheme for representing the gradual optical change that takes place under ion intercalation/deintercalation in EC NiO films is represented in equation (1),

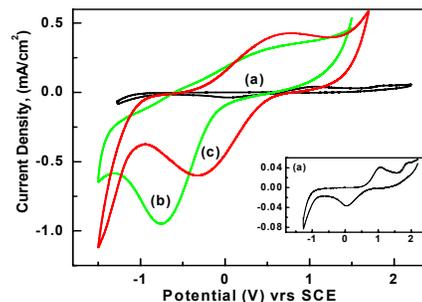
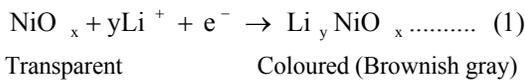
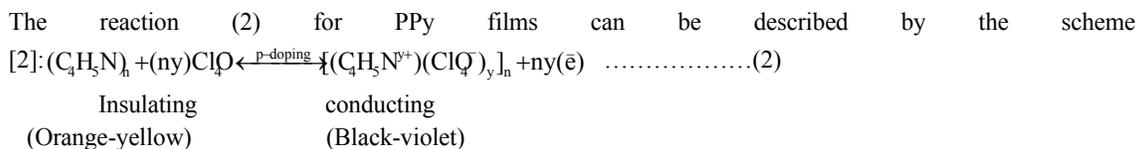


Fig.1

Figure 1. Cyclic voltammogram recorded in 1M LiClO4+PC electrolyte for (a) NiO (also shown in inset), b) PPy and c) NiO/PPy sample. The potential is swept from +2 to -1.2 V (vs SCE) for NiO and +1.5 to -1.5 V (vs SCE) for PPy and NiO/PPy at the scan rate of 20mV/s



The shape of the CV of NiO/PPy film (fig. 1 curve (c)) is very similar to the CV of PPy films having cathodic peak at -0.32 V (vs SCE) and anodic peak at +0.65 V (vs SCE) but with less current density, which indicates the presence of NiO. NiO/PPy shows electrochromism with colour changes from brown-yellow to black-violet (figure 2c) which represents that PPy plays leading role in EC of NiO/PPy.

The cyclic voltammograms were recorded in the range from -1.5 to 2.2 V (vs SCE) in 1M LiClO<sub>4</sub> + 1mM PC solution at 20 mV/s. Fig. 3 shows the CVs recorded for NiO, PANI and NiO/PANI films. The transition from NiOx to LiyNiOx after intercalation and deintercalation of Li<sup>+</sup> ions causes charge transfer from Ni<sup>+3</sup> to Ni<sup>+2</sup>. Due to charge transfer from Ni<sup>+2</sup> (transparent figure 4a) to Ni<sup>+3</sup>, films get coloured (brownish gray fig. 4a). PANI films shows electrochromism with color changes from pale yellow (leucomeraldine base at -0.3 V vs SCE)-dark green (emeraldine salt at 0.2 V vs SCE) - purple (pernigraniline at 0.9 V vs SCE) in the reduced states to - dark blue (nigraniline at 0.4 V vs SCE) dark green (emeraldine salt at 0.1 V vs SCE)-light green (photomeraldine at -0.7 V vs SCE) in the oxidized states (fig. 4b). The shape of the CVs (fig. 3) of NiO/PANI films is very similar to the CV of PANI films [3-5] which represents that PANI plays a lead role in EC of NiO/PANI. It gives same colouration as mentioned above in PANI except pernigraniline at 0.8 V vs SCE (fig. 3). The chromism showed by NiO/PANI films is shown in fig. 4c.

The switching characteristics of the NiO/PPy composite films were analyzed by monitoring the chronoamperometry. NiO exhibits slower response speed with about 1.7s for colouration (oxidation) and 2s for bleaching (reduction) kinetics. The response speed is much faster in case of PPy samples (145ms for colouration and 300ms for bleaching). The NiO/PPy samples exhibit much faster response speed as compared to pure NiO but almost similar to that of the PPy. This evinces dominant role of PPy, as far as response speed is concerned. This is not very surprising as our NiO samples are relatively more compact. The response times for oxidation and reduction were found to be 60 and 20 ms respectively. The switching speeds are better than reported by X. H. Xia et al (110 ms for NiO/PANI films) [6] but slower than those obtained by Lacroix et al (100 μs for NiO/PANI films) [7]. The switching speed (response time) is dependent on several factors such as applied potential, film thickness and electrolyte conductivity. Our samples NiO/PANI are about 340nm thick and tested in 1M LiClO<sub>4</sub> + 1mM PC which has lower electrolyte conductivity [6]. The fastest switching speeds will allow the most versatility in application and it can be used in display devices where the switching speeds of milliseconds or less may be required.

Fig.5 (a-c) shows the transmission spectra of the NiO, PPy and NiO/PPy films under its coloured and bleached states. The transmittance of NiO film is c/b at ±0.7 V vs SCE is shown in fig. 8a. The coloration efficiency (CE), an important parameter to probe the potential of the material as an EC material, was calculated at 633 nm by

using following relations:

$$CE_{\lambda=630nm} = \frac{(\Delta OD)_{630nm}}{Q_i} \text{-----(3)}$$

where  $(\Delta OD)_{630nm} = \ln(T_b/T_c)$ , and  $Q_i$  = charge intercalated. The change in optical density ( $\Delta OD$ ) is found to be 0.72 at 630 nm for the NiO films. The CE of NiO in the reduced and oxidized states is found to be 107cm<sup>2</sup>/C [8]. The optical behaviour of PPy degrades severely during initial c/b cycling. Fig. 5b shows transmittance change during initial cycling and found that  $\Delta OD$  changes from 0.7 to 0.45, causing CE to degrade from 181 to 117 cm<sup>2</sup>/C, within first 5 c/b cycles. Overall, the PPy sample could remain stable only upto 500 c/b cycles. The optical density of NiO/PPy films found to be 1.43 (fig. 5c) at 630 nm. The CE of NiO/PPy in the reduced and oxidized states is found to be 358 cm<sup>2</sup>/C ( $\Delta OD = 1.43$ ,  $Q_i = 4 \text{ mC/cm}^2$ ). The value was also calculated after 10,000 c/b cycling, which is 299 cm<sup>2</sup>/C. These values of  $\Delta OD$  and CE are much higher than those obtained from inorganic EC materials (CE < 100cm<sup>2</sup>/C) [9, 10] and comparable to that of inorganic-organic composite film ( $\Delta OD = 0.49$  and CE =208 cm<sup>2</sup>/C) [11]. Thus when the film of NiO/PPy is formed, the optical density is found to be enhanced appreciably without hampering its electrochemical stability.

Fig. 6 shows the UV-vis transmission spectra of the NiO, PANI and NiO/PANI composite films under different applied potentials. The EC mechanism as well as transmittance of NiO consisting of the transition metal was qualitatively explained by the band structure of the film [12,13]. The outer shell electrons in the nickel atoms are 3d<sup>8</sup>, 4s<sup>2</sup>. In chemical bonding of the EC film d level split into t<sub>2g</sub> and e<sub>g</sub> bands. It is due to the band gap that the optical absorbing ability changes. When t<sub>2g</sub> band is full, the electrons jumping probability from the t<sub>2g</sub> band to e<sub>g</sub> is very small that no photons can be absorbed in irradiation due to the energy band gap. This corresponds to the bleached state. While for the coloured state, the t<sub>2g</sub> band is not fully occupied. The film shows strong absorbing ability due to the inner band absorbing mechanism [14].

The transmittance of NiO film is  $c/b$  at  $\pm 0.7$  V vs SCE is shown in fig. 8a where the change in optical density ( $\Delta OD$ ) is found to be 0.72 at 630 nm. The optical density of PANI films is found to be 0.72 (fig. 6(b)) at 630 nm. The first absorption band at 375 nm arises from  $\pi-\pi^*$  transition of the benzenoid ring and the 490 nm band has been identified as due to the charge transfer transition ( $n-\pi^*$ ) from the HOMO of the benzenoid ring (non-bonded nitrogen lone pair) to the LUMO ( $\pi^*$ ) of the quinoid ring. The transmittance of NiO/PANI is observed similar to PANI having nearly same potentials but the intensity of transmittance decreases. This confirms that the dominant electrochromic contribution for this system is from PANI. The optical density of NiO/PANI films found to be 1.27 (fig. 6(c)) at 630 nm. Thus when the composite film of NiO/PANI is formed, the optical density is found to be enhanced from which we can conclude that the doping level of NiO/PANI increases. The CE of NiO/PANI in the reduced and oxidized states is found to be  $85\text{cm}^2/\text{C}$ .

#### IV. CONCLUSION

An electrochromic NiO/PPy and NiO/PANI film were assembled with a configuration of FTO/NiO/PPy and FTO/NiO/PANI. It is further characterized for its electrochromic and optical performance in  $\text{LiClO}_4+\text{PC}$ . The CE of the NiO/PPy film was observed to be  $358\text{cm}^2/\text{C}$ . These results were suitable to operate the device with perceptible color changes from brown-yellow in the reduced state to black-violet in the oxidized state in the potential range from  $-1.5$  to  $+1.5\text{V}$  (vs SCE). The response time of the film for coloring and bleaching process were found to be 200 and 309 ms, respectively. This indicates the faster insertion and deinsertion kinetics. The NiO/PPy film thus exhibits enhanced EC property owing to the chemical bonding between them.

The CE of the composite NiO/PANI film was observed to be  $85\text{cm}^2/\text{C}$ . These results were suitable to operate the device with perceptible color changes from yellow to green in the potential range from  $-1.5$  to  $+2.2$  V. The device changes colours from yellow to light green with intermediate steps of green, violet, blue and dark green. The response time of the film for coloring and bleaching process were found to be 60 and 20 ms, respectively. This indicates the faster insertion of  $\text{PANI}+\text{ClO}_4^-$  and deinsertion of  $\text{Li}^+$  ion from NiO. The composite NiO/PANI film exhibits enhance electrochromic property of NiO film and improve stability of the PANI films.

#### REFERENCES

- [1] P. Gomez Romero, "Hybrid Organic-Inorganic Materials", *Adv. Mater.* 13 (2001) 163.
- [2] S. Panero, S. Passerini, "Conducting Polymers: New electrochromic materials for advanced optical devices", *B. Scrosati, Mol. Cryst. Liq. Cryst.* 229 (1993) 97.
- [3] C. H. Yang, T. C. Wen, "Polyaniline Derivative with External and Internal Doping via Electrochemical Copolymerization of Aniline and 2,5-Diaminobenzenesulfonic Acid on  $\text{IrO}_2$ -Coated Titanium Electrode", *J. Electrochem. Soc.* 141(1994) 2624.
- [4] C. H. Yang, T. C. Wen, "Modified Polyaniline via Electrochemical Copolymerization of Aniline and para-Phenylenediamine Derivatives", *J. Electrochem. Soc.* 144 (1997,) 2078.
- [5] J. Yue, A. Epstein, "XPS Study of Self-Doped Conducting Polyaniline and Parent Systems," *J. Macromolecules* 24 (1991) 4441.
- [6] W.K. Lu, R.A. Elsenbaumer, "The Corrosion Protection of Metal by Conductive Polymers II—Pitting Corrosion," *Annu. Tech. Conf. Soc. Plast. Eng.* 56 (2)(1998) 1276.
- [7] Marco J. F., Gancedo J. R., Nguyen C. H., Del C. M., Gautier J.L., "Characterization of  $\text{Cu}_{1.4}\text{Mn}_{1.6}\text{O}_4/\text{PPy}$  composite electrodes " *Solid state ionics*, 177(2006)1381.
- [8] AC Sonavane, AI Inamdar, PS Shinde, HP Deshmukh, RS Patil, PS Patil, "Efficient electrochromic nickel oxide thin films by electrodeposition", *Journal of Alloys and Compounds* 489 (2)(2010), 667-673
- [9] C. Avino, S. Panero, B. Scrosati, "An electrochromic window based on a modified polypyrrole/nickel oxide combination" *J. Mater. Chem.*, 1993, 3(12), 1259.
- [10] C. G. Granqvist, *Handbook of Inorganic Electrochromic Materials*, Elsevier, Amsterdam, 1995.
- [11] X. H. Xia, J. P. Tu, J. Zhang, X. H. Huang, X. L. Wang, W. K. Zhang, H. Huang, "Multicolor and fast electrochromism of nanoporous NiO/poly(3,4-ethylenedioxythiophene) composite thin film" *Electrochemistry Communications* 11 (2009) 702.
- [12] C. G. Granqvist, "Electrochromic oxides: a bandstructure approach" *Sol. Energy Mater. Cells.* 32 (1994) 369.
- [13] C. Bechinger, S. Herminghaus, P. Leiderer, "Photoinduced doping of thin amorphous  $\text{WO}_3$  films", *Thin Solid Films*, 239 (1994) 156.
- [14] Y. Z. Xu, M. Q. Qui, S. C. Qui, J. Dai, G. J. Cao, H. H. He, J. Y. Wang, "Electrochromism of  $\text{NiO}_x\text{Hy}$  films grown by DC sputtering" *Sol. Energy Mater. Sol. Cells*, 45 (1997) 105.

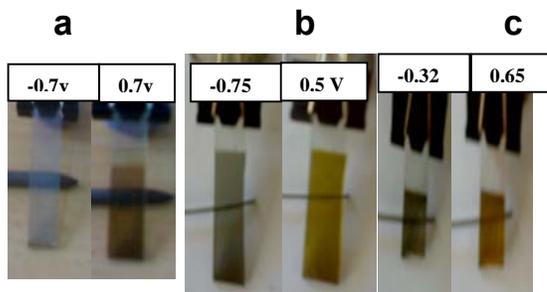


Figure2. Photographs of a sample a) NiO b) PPy c) NiO/PPy under different applied potentials

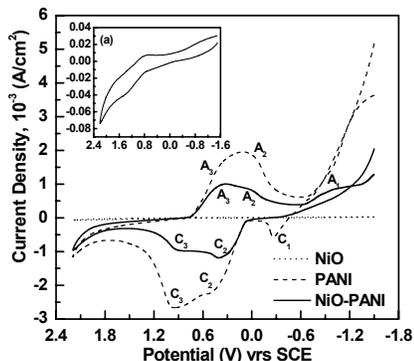
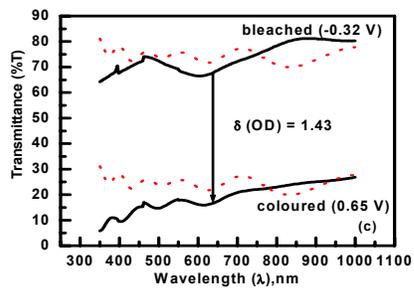
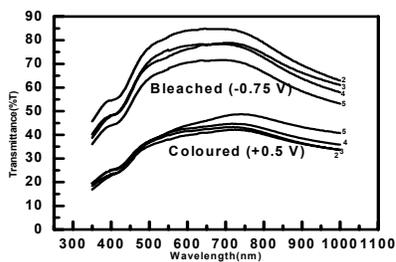
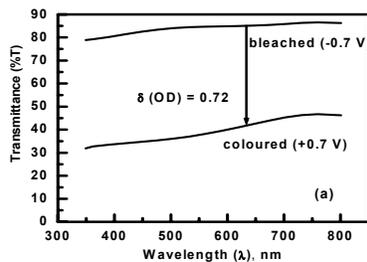


Figure 3. Cyclic voltammogram recorded in 0.1M LiClO4+PC electrolyte for NiO, PANI and NiO/PANI sample at 20mV/s scan rate.



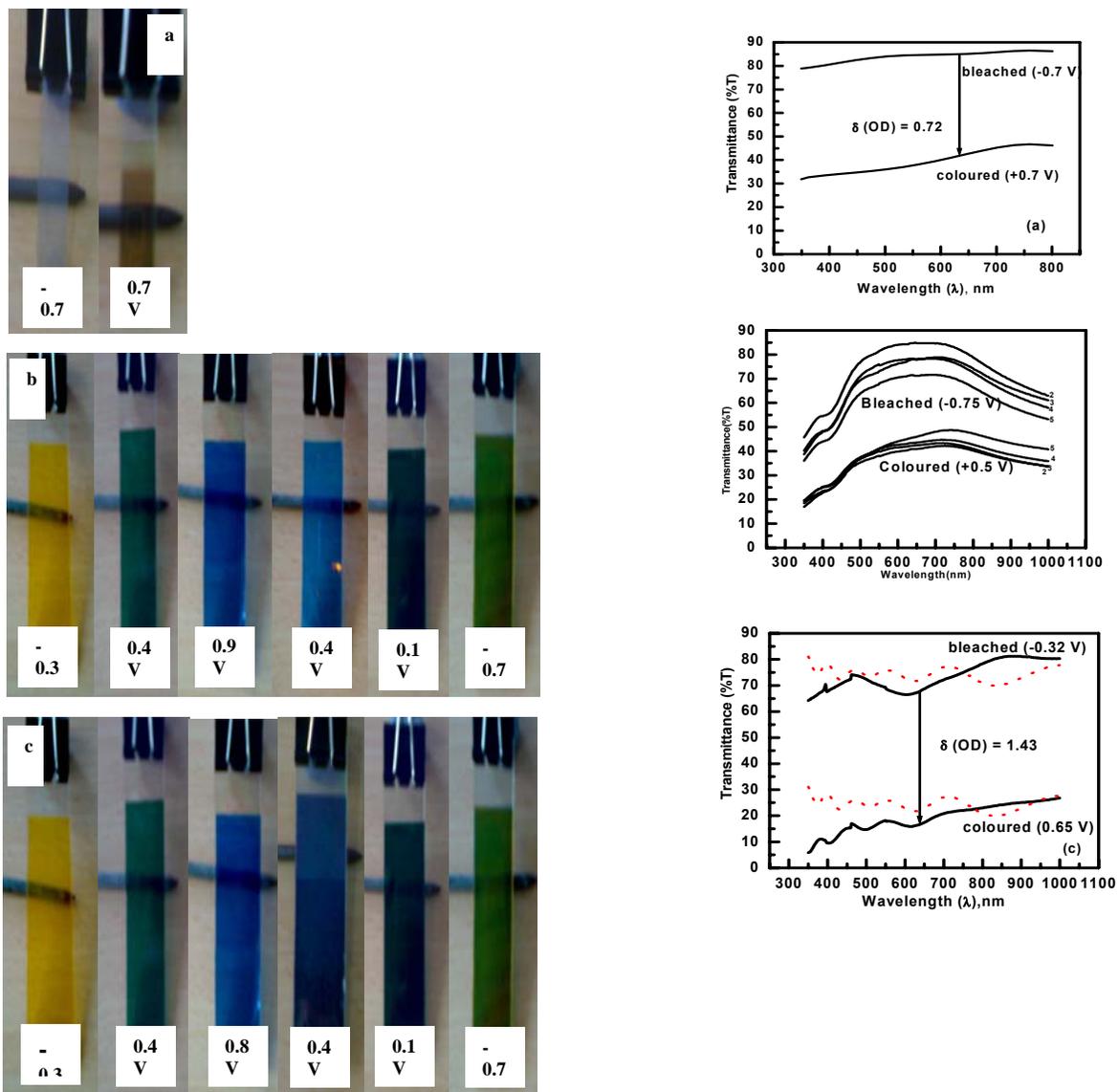


Figure 4. Photographs of a sample a) NiO b) PANI c) NiO/PANI under different applied potentials

Figure 5. Optical transmittance c/b at various potentials vs SCE in 1M LiClO<sub>4</sub> +PC electrolyte for 60 s of a) NiO recorded in the wavelength range 350 to 800 nm b) PPy within first five c/b cycles recorded in the wavelength range 350 to 1000 nm and (c) NiO/PPy film in the wavelength range 350 to 1000 nm where dots represent the transmittance after 10000th c/b cycle.

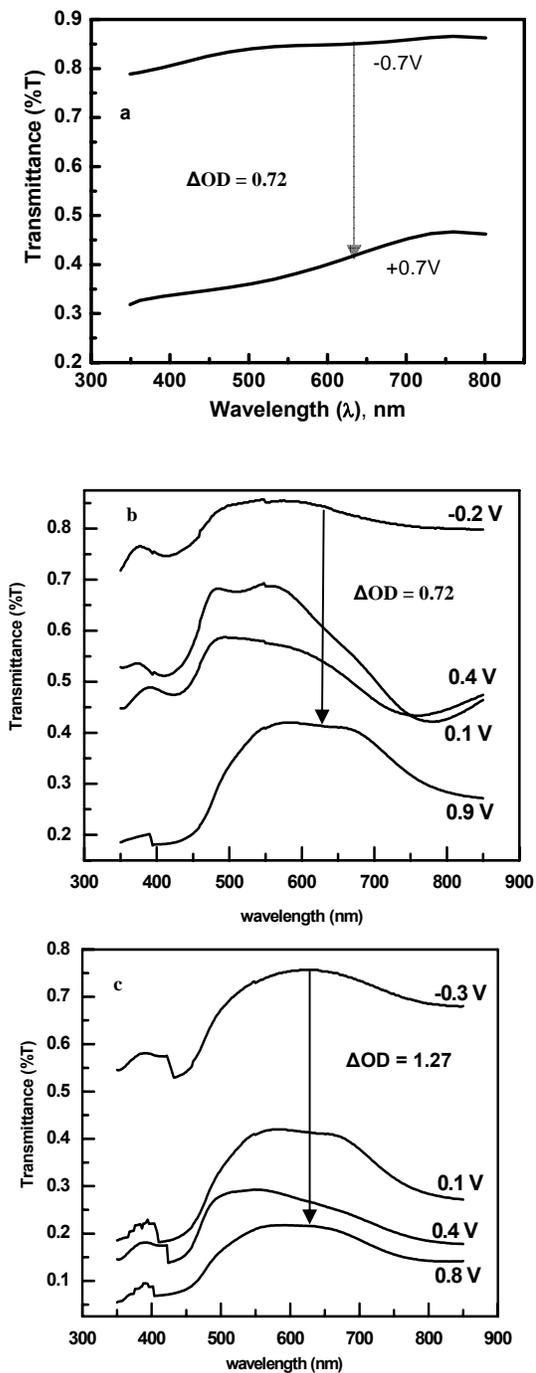


Figure 6. Optical transmittance a) NiO b) PANI and c) NiO/PANI film coloured/bleached at various potentials