VNU Journal of Science: Mathematics – Physics, Vol. 37, No. 2 (2021) 1-7

VNU Journal of Science: Mathematics - Physics

Journal homepage: https://js.vnu.edu.vn/MaP

Original Article

Electrochromic Properties of PANI/TiO_2 Nanocomposite Films Prepared by Electropolymerization

Nguyen Thi Khanh Van, Tran Si Trong Khanh, Vu Thi Thao, Nguyen Duc Cuong, Nguyen Phuong Hoai Nam, Nguyen Nang Dinh*

VNU University of Engineering and Technology, 144, Xuan Thuy, Cau Giay, Hanoi, Vietnam

Received 15 October 2020
Revised 16 November 2020; Accepted 30 November 2020

Abstract: PANI/nc-TiO_2/ITO composite films were prepared by electrochemical method where the monomer aniline was polymerized onto nano-porous TiO_2/ITO films (PANI/nc-TiO_2/ITO). The PANI/nc-TiO_2 heterojunctions were formed in the composite films due to the insertion of PANI in nano-porous TiO_2 particles. PANI/ITO films exhibited a reversible electrochromic display (ECD) performance when cycled in 0.1M $LiClO_4$ + propylene carbonate. The response times of the electrochromic coloration and bleaching of the PANI/nc-TiO_2/ITO electrode were 15 s and 20 s, respectively. Electrochromic efficiency of the films reached a value as large as 12.25 $cm^2 \times C^{-1}$. Taking advantage of the large EC efficiency and electrochemical stability as well as the simplicity of the fabrication process, PANI/nc-TiO_2 composite films can be used for preparation of electrochromic smart windows, in term of the large-area production in particular.

Keywords: Electrochromic device, PANI/nc-TiO_2, Electrochemical deposition, Cyclic voltammogram, Coloration efficiency.

1. Introduction

Electrochromism (EC) is the phenomenon where the color or opacity of a material (usually in thin film form) changes when a polarized voltage is applied. Electrochromic smart windows, thus can block ultraviolet, visible or near infrared radiations. EC properties have been found in almost all the transition-metal oxides and their properties have been investigated extensively [1]. These oxide films can be coloured anodically (Ir, Ni) or cathodically (W, Mo). Recently Granqvist et al. [2] have made a comprehensive review of nanomaterials for benign indoor environments. In that report, the authors show

*Corresponding author:
Email address: dinhnn@vnu.edu.vn

https//doi.org/ 10.25073/2588-1124/vnumap.4614

the characteristic data for a 5×5 cm^2 flexible EC foil incorporating WO_3, and NiO modified by the addition of a wide bandgap oxide such as MgO or Al_2O_3, PMMA-based electrolyte, and ITO films. Durability of the EC devices was demonstrated in performing several tens of thousands of coloration/bleaching cycles, and the device optical properties were found to be unchanged for many hours. Dinh et al. [3] pointed out that WO_3/TiO_2 films prepared by the doctor-blade followed by electrochemical deposition possessed both the better electrochromic performance and durability. The coloration of WO_3 deposited on indium-tin-oxides (ITO) substrates (WO_3/ITO) in 2M HCl was less than 1 sec and the maximum coloration efficiency (CE) at 630 nm was 22 $cm^2 \times C^{-1}$ [4]. However, the HCl electrolyte is not suitable for practical use. The Au-doped WO_3 films were made by a dip-coating technique [5]. Beydaghyan *et al* [6] showed that porous and nanostructured thick WO_3 films could produce a high CE. Thummarungsan et al. [7] prepared polyaniline (PANI) copolymer films via solution casting on ITO plastic substrate. The PANI-copolymer/ITO electrode has electrochromic display of the inverse change of green-to-blue light. We also prepared PANI/ ITO by using electropolymerization of aniline in a dilute H_2SO_4 solution [8]. As-prepared PANI films have a bell-like nanoporous structure. Both the PANI-copolymer/ITO and PANI/ITO possess a coloration efficiency ranging from 8.0 to 9.0 $cm^2 \times C^{-1}$. With such porous films, for a long exposed performance time, the durability of the devices was limited, making the ECD less satisfying for smart windows applications.

With the aim to improve the CE of the ECD performance and to enhance the stability of the EC devices, we used electrochemical polymerization for depositing PANI films onto nc-TiO_2. Morphology, ion exchange and electrochromic properties of the films were also presented in this paper

2. Experiment and Method

To prepare nanostructured TiO_2/ITO films, a doctor blade technique was used following the process reported in [9]. A glass slide coated with a 0.25 μm thick ITO film with a sheet resistance of 10 Ω/□ and a transmittance of 90% was used as a substrate where the the working area was as large as 10 cm^2. A colloidal solution of 15 wt. % nanoparticles (15 nm in size) of titanium oxide (Nyacol Products) in water was prepared Then the solution was filled in the slot on the ITO electrode and spread along the tapes. The samples were let for drying during 15 min, then put to a furnace maintained at 450°C for 1 hour to recrystallize the nc-TiO_2 films.

Then PANI/nc-TiO_2/ITO films were deposited by electropolymerization method using a solution of the pure reagent grade aniline and sulphuric acid (H_2SO_4) as reported in [8]. The electrochemical processes were carried-out by using a Potentiostat PGS-30 in a standard three-electrode cell, where nc-TiO_2/ITO served as working electrode (WE), Ag/AgCl as reference electrode (AAE) and a platinum grid as counter electrode (CE). The electrolyte used for the electropolymerization was composed of aqueous solution of 0.1 M aniline and 0.5M dopant sulphuric acid. PANI thin films were electropolymerized by sweeping the potential between -0.20 V and +1.20 V/AAE for 10 numbers of scans. All the experiments were performed at room temperature without stirring. The as-deposited PANI/ITO films were dried in gaseous nitrogen and kept in a clean glove-box before use. The electrochromic performance was carried out on the same PGS-30 potentiostat, using solution of 0.1M $LiClO_4$ in propylene carbonate for electrolyte.

The PANI films electropolymerization process in H_2SO_4 solution depends on the concentration of H_2SO_4, the scan rate and the range of the potentials used. Figure 1 shows typical cyclic voltammograms (CVs) of the best electropolymerized PANI films. The electrolyte contains 0.1M aniline monomer with 0.5M concentration of H_2SO_4. The CVs were recorded for 10 successive cycles at a scan rate of 50 mV/s for potential range from -0.1 to +0.6 V/AAE. We observed the decrease in growth rate upon repeating

the potential cycle [10] where the authors explained this phenomenon by the poor electrochemical activity of the PANI film. After completing 10 cycles, greenish-colored thin films were deposited which confirms the formation of emeraldine state (ES) of PANI.

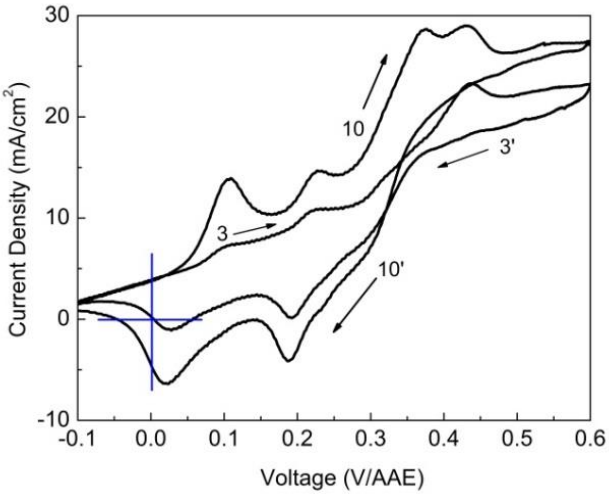

Figure 1. CV curves of a PANI/nc-TiO_2/ ITO film made by electropolymerization in 0.1M aniline and 0.5M H_2SO_4 solution by CV-cycling with a rate of 50 mV/s: (3-3') – the third cycle and (10-10') – the 10-th cycle.

3. Result and Discussion

3.1. Film Morphology

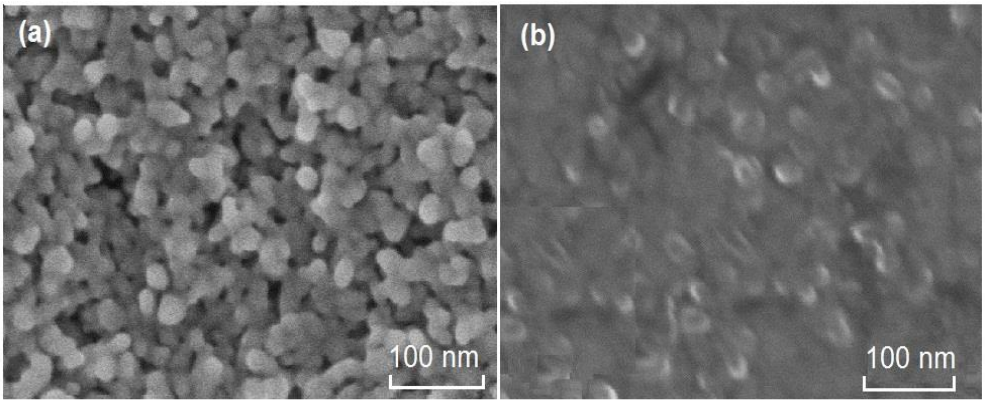

Figure 2. FE-SEM micrographs of the surfaces of a nc-TiO_2 (a) and a PANI/nc-TiO_2 film (b). The thickness of the film d = 450 nm

Bright-field micrographs of the samples is shown in Figure 2. The thickness of the composite film was determined by the point-to-point technique, d ~ 450 nm. The surface of the doctor-blade deposited sample clearly shows the nanoscale porosity of the TiO_2 film (Figure 2a). The electropolymerization of PANI resulted in the filling-up of PANI chains into the pores of the nanostructured TiO_2 structure. As a result, numerous PANI/nc-TiO_2 heterojunctions were created in the composite film (Figure 2b).

3.2. Electrochemical Property

Figure 3 shows the cyclic voltammetry (CV) curve in 0.1M$LiClO_4$ + PC of a PANI/nc-TiO_2/ITO film served as the working electrode (WE) where the CV spectra was recorded at the fifth cycle. This is a typical curve for the films of 450nm thickness prepared by our studies

From this figure one can see a nearly symmetrical shape of the CV spectra toward the coordinates (x = 0.60; y = 0.16). In the positive sweep direction (PSD) a peak of the anodic current density corresponding to a value of ca. 0.55 mA was obtained at a potential of 1.05 V/AAE. A negative value (– 0.21 mA) of the peak in the negative sweep direction (NSD) was obtained at a potential of 0.36 V/AAE. The symmetrical CV proves a good reversibility of the processes of (ClO_4^-) ion insertion / extraction from the electrolyte into /out of the working electrode (WE). Since PANI/nc-TiO_2/ITO consists of two electrochromic materials, namely polymeric PANI and inorganic nc-TiO_2, electrochromic performance can be expressed by a double overall reaction, as follows.

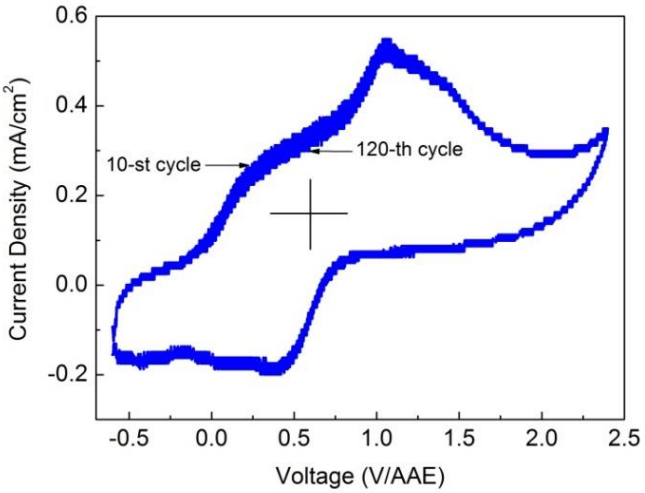

Figure 3. Cyclic voltammetry spectra of PANI/nc-TiO_2/ITO cycled in $LiClO_4$+PC (scanning rate ν = 100 mV/s).

During the oxidation (PANI/nc-TiO_2/ITO is positively polarized), the ClO_4^- ions from $LiClO_4$/PC electrolyte solution insert in to and Li^+ ions extract out off the WE. The first double reaction (corresponding to the bleaching state) can be expressed as [11]:

$$(ANI)n + ny(ClO_4^-) \rightarrow [(ANI+) + y(ClO4^-)]n + nye^- \quad (1)$$

(Blue) (Light green)

where n is the number of repeated units and y is the stoichiometric number of the counter ion;
and as [12,13]:

$$Li_xTiO_2 \rightarrow TiO_2 + x(Li^+ + e^-) \quad (2)$$

(Blue) (Transparent)

During the reduction (PANI/nc-TiO_2/ITO is negatively polarized), the ClO_4^- ions of $LiClO_4$/PC electrolyte solution were excluded the WE, whereas Li^+ ions were inserted in to it. The second double reaction (corresponding to the coloration state) is described by two above equations with the inverse

direction of the arrows. Thus, combining Eqs. (1) and (2), one can describe the electrochromic performance of PANI/nc-TiO_2/ITO electrode by an overall reaction, as follows:

$$\underset{\text{(Light green)}}{PANI\text{-}ClO_4^- /TiO_2} + Li^+ \leftrightarrow \underset{\text{(Blue)}}{PANI/Li_xTiO_2} + ClO_4^- \quad (3)$$

The electrochromic coloration of the PANI/nc-TiO_2/ITO occurred due to the simultaneous double possesses of insertion and extraction of ClO_4^- and Li^+ ions, respectively. In our case, for the composite WE during the performance, the electrochromic display is due to a reversible light-green and blue colour change. This is a specific difference in PANI/nc-TiO_2 based EC devices compared to that of the single WO_3 or TiO_2 films displaying a reversible transparent-to-blue change.

3.3. Electrochromic Performance

For a sample with a 450 nm-thick PANI/nc-TiO_2 film (WE), the *in situ* transmission spectra, obtained during coloration at a polarized potential of –0.5 V/ AAE are given in **Figure 4**.

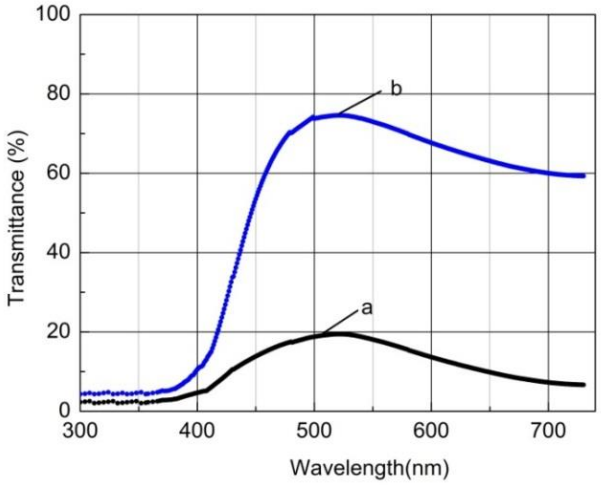

Figure 4. Transmittances of the PANI/nc-TiO_2 film. The oxidizing potential and reducing potential were set +0.3 V/AAE and - 0.5 V/AAE, respectively. Curve "a" is the colored state and curve "b" is bleached state.

From Figure 4 one can see a large difference in transmittance spectra in the visible range of the film between the colored (curve "a") and bleached (curve "b") states. In about 15s, the transmittance at λ = 550 nm from ~ 70% decreased to ~ 16% with the colored state, corresponding to bias potential – 0.5 V/ AAE. With a polarized potential of + 0.3 V/AAE, the WE bleached in 20s. This result indicates that the electrochemically deposited PANI/nc-TiO_2 films exhibited a good reversibility of the EC performance. From the above mentioned results for the ECDs with heterojunctions of PANI/nc-TiO_2, it is seen that the efficient coloration can be achieved due to a double coloration process, as shown in Eqs. (1) and (2).

The electrochromic coloration efficiency (η) was calculated using well-known expression relating the efficiency with the optical density, consequently the transmittances of coloration (T_c) and bleaching states (T_b), and the insertion charge (Q), as follows [14]:

$$\eta = \frac{\Delta OD}{Q} = \frac{1}{Q} ln\left(\frac{T_b}{T_c}\right) \quad (4)$$

In our experiments Q = 0.12 mC×cm^{-2}. At a wavelength of 550 nm, T_b = 70% and T_c = 16%, thus the coloration efficiency was found to be of ~ 12.25 cm^2×C^{-1}. In the visible range of wavelengths, η of the PANI/nc-TiO_2 device was found to be larger than that of the PANI/ITO device made by electropolymerization [8] as well as made by electrochemistry [15].

4. Conclusion

PANI/nc-TiO_2/ITO composite films were prepared by electropolymerization of monomer aniline onto nc-TiO_2/ITO films which were made from the doctor-blade technique. By embedding PANI in porous TiO_2 nanoparticles, PANI/nc-TiO_2 heterojunctions were formed in the composite films. The coloration efficiency and electrochemical stability of the PANI/nc-TiO_2 films were considerably improved. The response times of the ECD coloration/bleaching and electrochromic efficiency of PANI/nc-TiO_2/ITO were 15–20 s and 12.25 cm^2×C^{-1}, respectively. Since a large-area PANI/nc-TiO_2/ITO electrode can be prepared by the doctor-blade method, the PANI/nc-TiO_2/ITO films contribute a good candidate for smart window applications, taking advantage of its large efficiency and electrochemical stability as well as the simplicity of the fabrication process.

Acknowledgement

This work has been supported by VNU University of Engineering and Technology under Project number CN20.05.

References

[1] C. G. Granqvist, Electrochromics for smart windows: Oxide-based thin films and devices, Thin Solid Films Vol. 564, No. 1, 2014, pp. 1-38, https://doi.org/10.1016/j.tsf.2014.02.002

[2] C. G. Granqvist, A. Azens, P. Heszler, L. B. Kish, L. Österlund, Nanomaterials for benign indoor environments: Electrochromics for smart windows, sensors for air quality, and photo-catalysts for aircleaning, Sol. Energy Mater. Sol. Cells, Vol. 91, Issue 4, 2007, pp. 355-365, https://doi.org/10.1016/j.solmat.2006.10.011.

[3] N. N. Dinh, D. H. Ninh, T. T. Thao, V. V. Truong, Mixed Nanostructured Ti-W Oxides Films for Efficient Electrochromic Windows, J. Nanomater., Vol. 2012, Special Issue, 2012, Article ID 781236, https://doi.org/10.1155/2012/781236.

[4] L. Meda, R. C. Breitkopf, T. E. Haas and R. U. Kirss, Investigation of electrochromic properties of nanocrystalline tungsten oxide thin film, Thin Solid Films, Vol. 402, No. 1-2, 2002, pp. 126-130, https://doi.org/10.1016/S0040-6090(01)01598-X.

[5] N. Naseri, R. Azimirad, O. Akhavan and A.Z. Moshfegh, Improved electrochromical properties of sol–gel WO_3 thin films by doping gold nanocrystals, Thin Solid Films, Vol. 518, No. 8, 2010, pp. 2250-2257, https://doi.org/10.1016/j.tsf.2009.08.001.

[6] G. Beydaghyan, G. Bader, P. V. Ashrit, Electrochromic and morphological investigation of dry-lithiated nanostructured tungsten trioxide thin films, Thin Solid Films, Vol. 516, No. 8, 2008, pp. 1646-1650, https://doi.org/10.1016/j.tsf.2007.05.006.

[7] N. Thummarungsan and D. Pattavarakorn, Electrochromic Performances of Conductive Polyaniline Copolymer, Int. J. Chem. Eng. Appl., Vol. 5, Issue 2, 2014, pp. 176-180, https://doi.org/ 10.7763/IJCEA.2014.V5.373.

[8] D. H. Ninh, T. T. Thao, P. D. Long, N. N. Dinh, Characterization of electrochromic properties of polyaniline thin films electropolymerized in H_2SO_4 solution, Open J. Org. Polym. Mater., Vol. 6, Issue 1, 2016, pp. 30-37, https://doi.org/ 10.4236/ojopm.2016.61004.

[9] N. N. Dinh, N. M. Quyen, D. N. Chung, M. Zikova,V. V. Truong, Highly-efficient electrochromic performance of nanostructured TiO_2 films made by doctor blade technique, Sol. Energy Mater. Sol. Cells, Vol. 95, Issue 2, 2011, pp. 618-623, http://dx.doi.org/10.1016/j.solmat.2010.09.028.

[10] D. E. Stilwell, S. M. J. Park, Electrochemistry of Conductive Polymers II. Electrochemical Studies on Growth Properties of Polyaniline, J. Electrochem. Soc., Vol. 135, No. 9, 1988, pp. 2254-2262, http://dx.doi.org/10.1149/1.2096248.

[11] K. Y. Shen, C. W. Hu, L. C. Chang, K. C. Ho, A complementary electrochromic device based on carbon nanotubes/conducting polymers, Sol. Energy Mater. Sol. Cells, Vol. 98, March 2012, pp. 294-299, https://doi.org/10.1016/j.solmat.2011.11.020.

[12] T. Ohtsuka, M. Masud, N. Sato, Ellipsometric Study of Anodic Oxide Films on Titanium in Hydrochloric Acid, Sulfuric Acid, and Phosphate Solution, J. Electrochem. Soc., Vol. 132, No. 4, 1985, pp. 787-795, https://doi.org/10.1149/1.2113958.

[13] N. N. Dinh, N. T. T. Oanh, P. D. Long, M. C. Bernard, A. Hugot-Le Goff, Electrochromic properties of TiO_2 anatase thin films prepared by dipping sol-gel method, Thin Solid Films, Vol. 423, No. 1, 2003, pp. 70-76, https://doi.org/10.1016/S0040-6090(02)00948-3.

[14] P. M. S. Monk, R. J. Mortimer, D. R. Rosseinsky, Electrochromism: Fundamentals and Applications. VCH, Weinheim-New York-Basel-Cambridge-Tokyo – 1995. ISBN: 978-3-527-61536-0 (239 p).

[15] J. H. Kang, Y. J. Oh, S. M. Peak, S. J. Hwang, J. H. Choy, Electrochromic Device of PEDOT-PANI Hybrid System for Fast Response and High Optical Contrast, Sol. Energy Mater. Sol. Cells, Vol. 93, Issure 12, 2009, pp. 2040-2044, https://doi.org/10.1016/j.solmat.2009.08.007.