The Investigation of the Electrochromic Characteristics for the PANI Thin Film by Cyclic Voltammetry and Potentiostatic Method

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***Abstract*—The objective of this study is to investigate optical and electrochemical characteristics of Polyaniline (PANI)/indium tin oxide/glass (ITO/Glass) by cyclic voltammetry and potentiostatic method. The electrochromic behaviors of the PANI/ITO/Glass were performed in 0.1 M lithium perchlorate ($LiClO_4$) /propylene carbonate (PC) electrolyte. The PANI/ITO/Glass had the best optical characteristics and electrochemical characteristics when the deposited cycle and voltage of the PANI thin film were set for 10 times and -0.5 V~ +1.5 V, respectively. The coloration efficiency (η) of the PANI/ITO/Glass was 9.35 cm^2/C. Furthermore, the experimental results observed that the color of PANI/ITO/Glass was changed from Green (oxidation state) to Light Green (reduction state).**

***Index Terms*—Polyaniline, cyclic voltammetry, potentiostatic method, electrochromism, coloration efficiency**

I. Introduction

THE conjugated polymers are organic macromolecules, which consist of one or more backbone chains of alternating double and single bonds. Conjugated polymers have been widely used in variety of applications, such as polymer conductors [1], electronic components [2, 3], light-emitting diodes [4], batteries [5], and polymer electrochromic devices (PECDs) [6], because they exhibit several advantages, such as thermal stability, low cost and easy preparation.

Various methods have been proposed to deposit the conjugated polymers thin film, such as chemical and electrochemical polymerizations. The conjugated polymers prepared by chemical or electrochemical polymerization have received significant attention due to the wide range of electrical, electrochemical, and optical properties [7]. In this study, the thin film of the conjugated polymers was deposited on the indium tin oxide/glass (ITO/Glass) substrate by electrochemical polymerization. The advantages of electrochemical polymerization comparing with other methods include rapidity, simplicity, generation of the polymer directly on the electrode in the doped or undoped states, and easy controlled synthesis of these compounds [8]. According to these results, the preparation, characterization and application of electrochemically active and electronically conjugated polymeric systems are still investigated in electrochemistry [9].

Polyaniline (PANI) shows yellow color in the reduction state and green color in the oxidation state [10-13]. It can be applied to electrochromic displays [14]. According to the mentioned above, the electrochromic PANI thin film can be applied in display for green pixel.

In this study, the PANI thin film has been electrodeposited on the indium tin oxide/glass (ITO/Glass) substrate with the various deposition charges to optimize electrochromic property of the PANI thin film. Furthermore, the electrochromic property of the PANI thin film has been studied in a 0.1 M lithium perchlorate ($LiClO_4$)/propylene carbonate (PC) electrolyte solution, and color of the PANI

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thin film was switched between green (1.0 V (PANI vs. Platinum (Pt))) and yellow (-0.5 V (PANI vs. Pt)).

II. Experimental

A. Materials

Indium tin oxide/glass (ITO/Glass) substrate was manufactured by Sinonar Corp., Taiwan, and its sheet resistivity is 7 Ω/□. Aniline (ANI) solution, hydrogen chloride, (HCl) solution, lithium perchlorate ($LiClO_4$) powders and propylene carbonate (PC) solution were all purchased from Acros Organics Corp., USA.

B. Instrumentation

BioLogic potentiostat/Galvanostat (model SP-150, France) was used to electrodeposit the PANI thin film on the ITO/Glass and to perform cyclic voltammetry (CV) measurements, respectively. OTO Photonic Spectrometer (model SD1200-LS-HA, Taiwan) was used to measure transmittance of electrochromic thin film.

C. Preparation of the PANI Thin Film

In this study, the electrochromic PANI thin film have been deposited on the indium tin oxide/glass (ITO/Glass) substrate by cyclic voltammetry and potentiostatic method. The PANI thin film was deposited on the ITO/Glass by cyclic voltammetry in 1 M ANI and 2 M HCl with deionized (D. I.) water, and the potentials were set at -0.5 V ~ +1.5 V, the scan rate is 100 mV s^{-1}. The deposited times were controlled for 10, 20, 30, 40, 50 and 60 times, respectively. On the other hand, the PANI thin film was deposited on the ITO/Glass by potentiostatic polymerization in 1 M ANI and 2 M HCl with deionized (D. I.) water, and the potential was set at +1.5 V. The deposited time were controlled for 400, 800, 1200, 1600, 2000 and 2400 s, respectively. The PANI thin film electrodes were removed from the monomer/electrolyte solution after electrochemical polymerization and rinsed with 0.1 M HCl to produce cleaned surface without monomer. Fig. 1 was the schematic diagram of the electrochromic PANI device in this study.

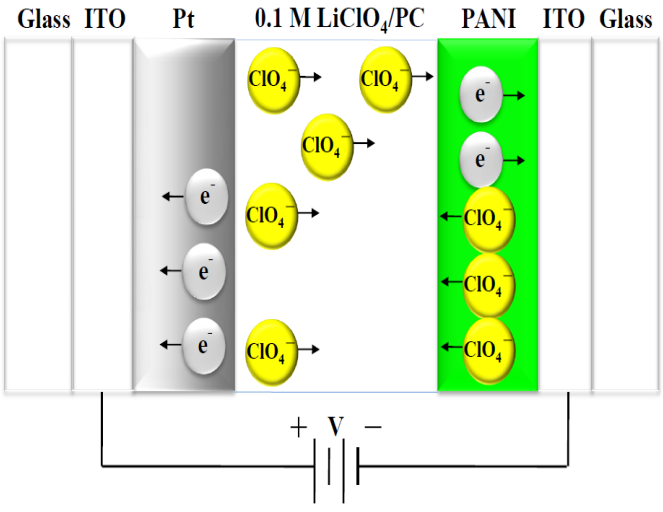

Fig. 1. Structure of electrochromic PANI device [15].

III. Results and Discussion

The PANI thin film was obtained by cyclic voltammetry and potentiostatic method. And the PANI thin film was obtained by electrochemical polymerization at potential slightly higher than the monomer oxidation onset potential, and obtained a homogeneous thin film on the ITO/Glass. The redox behavior of the ANI monomer was obtained in 1 M ANI and 2 M HCl with D. I. water by cyclic voltammetry, as shown in Fig. 2. An oxidation onset potential was obtained about 1.25 V. Because lower potential could not synthesize the ANI, the potential of polymerization of the PANI thin film was set at 1.5 V. The CV curves of the PANI thin film exhibited that the onset potential of oxidation of ANI was at +1.25 V in 1 M ANI and 2 M HCl with D. I. water, as well as, the oxidation peak of the PANI thin film at +0.75 V and reduction peak of the PANI thin film was at +0.15 V during the 20 cycles.

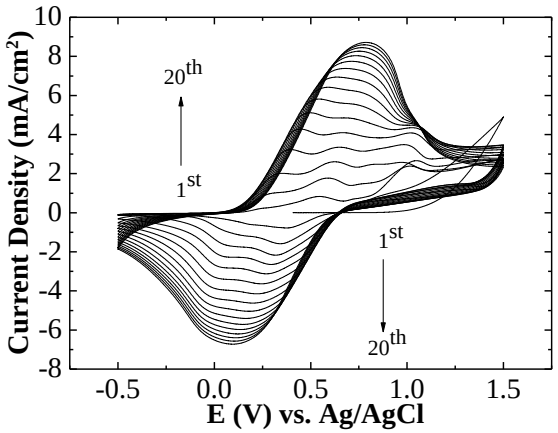

Fig. 2. Cyclic voltammograms of PANI thin film during electrodeposition (scan rate = 100 mV/s).

As shown in Fig. 3, the cyclic voltammetry of the PANI/ITO/Glass and the maximum current density was observed when the PANI thin film (the PANI/ITO/Glass with 10 times) was fabricated by cyclic voltammetry. During the oxidation (anodic peak at 0.75 V), the ClO_4^- ions of $LiClO_4$/PC electrolyte solution were injected from the PANI thin film. During the reduction (cathodic peak at −0.25 V), the ClO_4^- ions of $LiClO_4$/PC electrolyte solution were excluded the PANI thin film. The overall reaction, involving ion diffusion -in and -out of the polymer matrix to balance the charge, can be represented as in Eq. (1) for PANI [13],

$$(ANI)_n + ny(ClO_4^-) \longleftrightarrow [(ANI^+) + y(ClO_4^-)]_n + nye^- \quad (1)$$

(Light Green) (Green)

Where n is the number of repeated units and y is the stoichiometric number of the counter ion [13].

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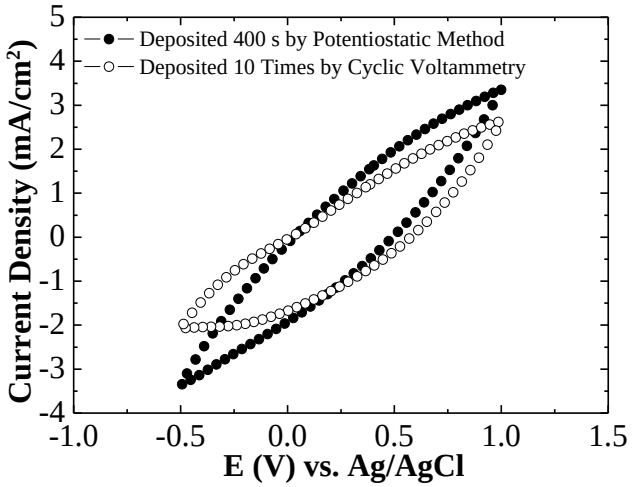

Fig. 3. Cyclic voltammograms of the PANI/ITO/Glass in 0.1 M $LiClO_4$/PC electrolyte solution with scan rate of 100 mV s^{-1} by different methods：●-Deposited 400 s by constant potential +1.5 V; ○ -Deposited 10 times by deposited voltage -0.5 V~ +1.5 V.

As shown in Fig. 4, the colored and bleached transmittances of the PANI/ITO/Glass were studied with 10 times and -0.5 V~ +1.5 V by cyclic voltammetry. The PANI/ITO/Glass was performed in 0.1 M $LiClO_4$ /PC electrolyte solution. The potentials were -0.5 V and +1.0 V. The solid shape and hollow shape were coloring and bleaching, respectively. The PANI/ITO/Glass has the maximum optical transmittance variation (ΔT(%)) which was 20 % at 550 nm.

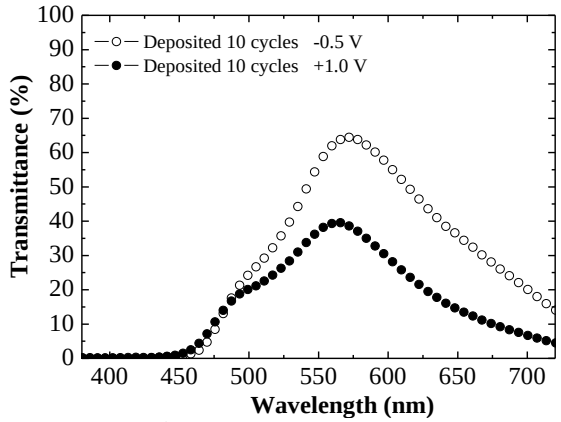

Fig. 4. Transmittances of the PANI/ITO/Glass (the PANI/ITO/Glass with 10 times) was immersed in 0.1 M $LiClO_4$/PC electrolyte solution, and the oxidizing potential and reducing potential were set +1.0 V and -0.5 V, respectively.

As shown in Fig. 5, the colored and bleached transmittances of the PANI/ITO/Glass were studied with 400 second and +1.5 V by potentiostatic method. The PANI/ITO/Glass was performed in 0.1 M $LiClO_4$ /PC electrolyte solution. The potentials were -0.5 V and +1.0 V. The solid shape and hollow shape were coloring and bleaching, respectively. The PANI/ITO/Glass has the maximum optical transmittance variation (ΔT(%)) which was 1 % at 550 nm.

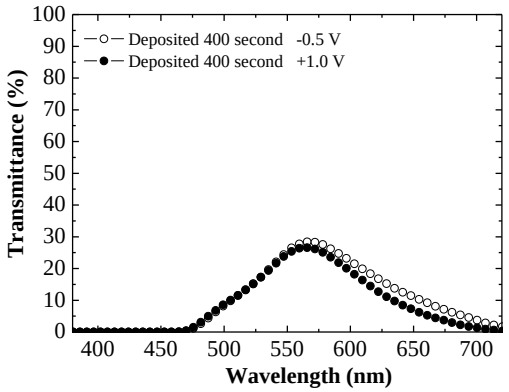

Fig. 5. Transmittances of the PANI/ITO/Glass (the PANI/ITO/Glass with 400 second) was immersed in 0.1 M $LiClO_4$/PC electrolyte solution, and the oxidizing potential and reducing potential were set +1.0 V and -0.5 V, respectively.

As shown in Fig. 6, the coloration efficiency (η) of the PANI/ITO/Glass with different fabricated parameters. The PANI/ITO/Glass had the best transmittance variation (20 %) when the deposited cycle and voltage of the PANI thin film were set for 10 times and -0.5 V~ +1.5 V, respectively. The coloration efficiency of the PANI/ITO/Glass was 9.35 cm^2/C. Compared with the above results, the coloration efficiency of the PANI/ITO/Glass was higher than other literatures [16-18], as summarized in TABLE I.

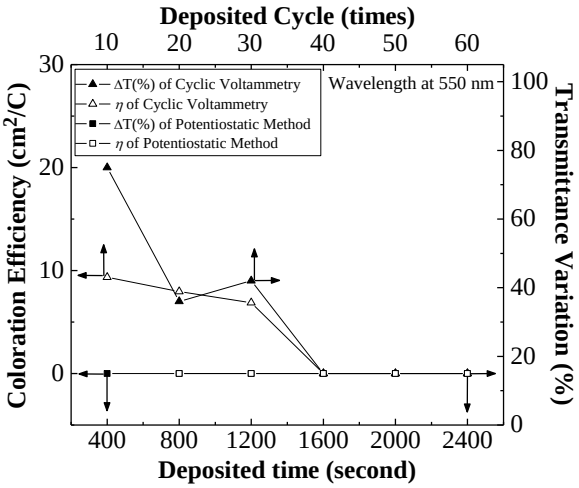

Fig. 6. Transmittance variation and coloration efficiency of the PANI/ITO/Glass in 0.1 M $LiClO_4$/PC electrolyte solution between oxidizing potential (+1.0 V) and reducing potential (-0.5 V).

The variational colors of the electrochromic thin film were observed by the chromaticity coordinates of the commission internationale de l'Eclairage 1931 (CIE 1931). Fig. 7 shows the chromaticity coordinates of CIE of PANI/ITO/Glass (the colored and bleached transmittances of the PANI/ITO/Glass were studied with 10 times and -0.5 V~ +1.5 V by cyclic voltammetry) were performed in 0.1 M $LiClO_4$ /PC electrolyte solution. The PANI/ITO/Glass in yellow color state (reduction state) was at －0.5 V (PANI vs. Pt), and the chromaticity coordinate of the PANI/ITO/Glass was (0.28, 0.48). Green color state (oxidation state) of PANI thin film was at +1.0 V (PANI vs. Pt), and the chromaticity coordinate of the PANI/ITO/ Glass was (0.14, 0.54).

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TABLE I. COMPARISON OF THE COLORATION EFFICIENCY OF THE PANI/ITO/GLASS IN THIS STUDY AND PREVIOUS LITERATURES FOR ELECTROCHROMIC DEVICE.

Electrochromic Device	Method	Coloration Efficiency (cm^2/C)	Wavelength (nm)	Transmittance Variation ($\Delta T(\%)$)	Time of Manufacture	Cost of Manufacture	Ref.
PANI/ITO/Glass	Electrochemistry	9.35	550	20	short	low	In this study
PANI/ITO/Glass	Chemistry	42.80	550	41	long	high	[16] (2009)
PANI/G/Glass	Chemistry	39.60	550	45	long	high	[16] (2009)
PANI/ITO/Glass	Screen-Printed	52.00	550	N/A	long	high	[17] (2009)
POSS-PANI/ITO/Glass	Screen-Printed	69.00	550	N/A	long	high	[17] (2009)
PANI/ITO/Glass	Electrochemistry	6.20	550	N/A	short	low	[18] (2009)

N/A: Not Applicable

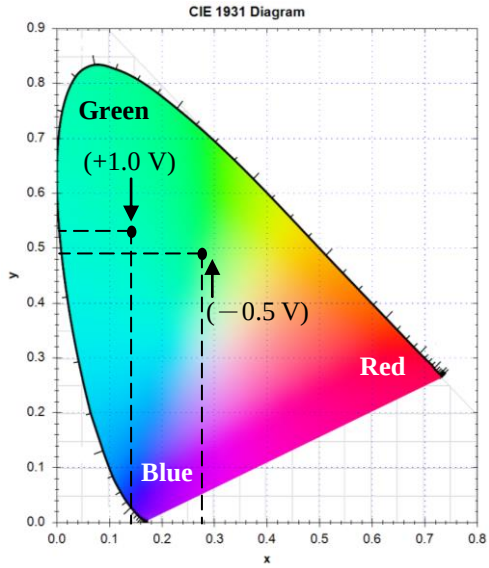

Fig. 7. Chromaticity coordinates of CIE of PANI/ITO/Glass (the colored and bleached transmittances of the PANI/ITO/Glass were studied with 10 times and -0.5 V~ +1.5 V by cyclic voltammetry) were performed in 0.1 M $LiClO_4$ /PC electrolyte solution.

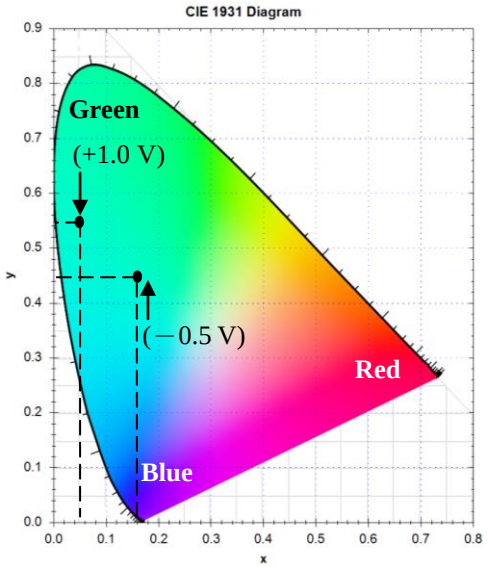

Fig.8.Chromaticity coordinates of CIE of PANI/ITO/Glass (the PANI/ITO/Glass were studied with 400 second and +1.5 V by potentiostatic method) were performed in 0.1 M $LiClO_4$ /PC electrolyte solution.

Fig. 8 shows the chromaticity coordinates of CIE of PMeT/ITO/Glass (the PANI/ITO/Glass were studied with 400 second and +1.5 V by potentiostatic method) was performed in 0.1 M $LiClO_4$ /PC electrolyte solution. The PANI /ITO/Glass in light green color state (reduction state) was at −0.5 V (PANI vs. Pt), and the chromaticity coordinate of the PANI/ITO/Glass was (0.16, 0.42). When dark green color state (oxidation state) of PANI thin film was at +1.0 V (PANI vs. Pt), and the chromaticity coordinate of the PANI/ITO/ Glass was (0.04, 0.44).

IV. Conclusions

The electrochromic PANI thin film has been successfully deposited on ITO/Glass by cyclic voltammetry and potentiostatic method. The PANI/ITO/Glass had the best transmittance variation (20 %) when the deposited cycle and voltages of the PANI thin film were set for 10 times and -0.5 V ~ +1.5 V, respectively. The coloration efficiency of the PANI/ITO/Glass was 9.35 cm^2/C. According to the experimental results, the electrochromic PANI thin film was prepared by cyclic voltammetry, which has the best transmittance variation and current density. Furthermore, the experimental results obtained the colors of the PANI/ITO/Glass were from Green (oxidation state) to Light Green (reduction state). According to the above results, the electrochromic PANI/ITO/Glass can be applied in display for green pixel.

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REFERENCES

[1] X. Crispin, F. L. E. Jakobsson, A. Crispin, P. C. M. Grim, P. Andersson, A. Volodin, C. van Haesendonck, M. Van der Auweraer, W. R. Salaneck, M. Berggren, "The origin of the high conductivity of poly(3,4-ethylenedioxy-thiophene)-poly(styrenesulfonate)(PEDOT-PSS) plastic electrodes," *Chem. Mater.*, vol. 18, pp. 4354-4360, 2006.

[2] H. Sirringhaus, T. Kawase, R. H. Friend, T. Shimoda, M. Inbasekaran, W. Wu, E. P. Woo, "High-resolution inkjet printing of all-polymer transistor circuits," *Sci.*, vol. 290, pp.2123-2126, 2000.

[3] H. E. Katz, J. Huang, "Thin-film organic electronic devices," *Annu. Rev. Mater. Res.*, vol. 39, pp. 71-92, 2009.

[4] I. D. Parker, "Carrier tunneling and device characteristics in polymer Light-Emitting Diodes," *J. Appl. Phys.*, vol. 75, pp. 1656-1666, 1994.

[5] S. R. Sivakkumar, J. Y. Nerkar, A. G. Pandolfo, "Rate capability of graphite materials as negative electrodes in lithium-ion capacitors," *Electrochim. Acta*, vol. 54, pp. 6844-6849, 2009.

[6] A. Yildirim, S. Tarkuc, M. Ak, L. Toppare, "Syntheses of electroactive layers based on functionalized anthracene for electrochromic applications," *Electrochim. Acta*, vol. 53, pp. 4875-4882, 2008.

[7] G. A. Sotzing, J. R. Reynolds, "Electrochromic conducting polymers via electrochemical polymerization of bis(2-(3,4-ethylenedioxy) thienyl) monomers," *Chem. Mater*, vol. 8, pp. 882-889, 1996.

[8] Y. Pang, X. Li, H. Ding, G. Shi, L. Jin, "Electropolymerization of high quality electrochromic poly(3-alkyl-thiophene)s via a room temperature ionic liquid," *Electrochim. Acta*, vol. 52, pp. 6172-6177, 2007.

[9] G. Inzelt, M. Pineri, J. W. Schultze, M. A. Vorotyntsev, "Electron and proton conducting polymers: recent developments and prospects," *Electrochim. Acta*, vol. 45, pp. 2403-2421, 2000.

[10] K. Sheng, H. Bai, Y. Sun, C. Li, G Shi, "Layer-by-layer assembly of graphene/polyaniline multilayer films and their application for electrochromic devices," *Polymer*, vol. 52, pp. 5567-5572, 2011.

[11] S. Xionga, F. Yangb, G. Ding, K. Y. Mya, J. Ma, X. Lu,"Covalent bonding of polyaniline on fullerene: enhanced electrical, ionic conductivities and electrochromic performances," *Electrochim. Acta*, vol. 67, pp. 194-200, 2012.

[12] H. Karami, M. G. Asadic, M. Mansoori,"Pulse electropolymerization and the characterization of polyaniline nanofibers," *Electrochim. Acta*, vol. 61, pp. 154-164, 2012.

[13] 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, pp. 294-299, 2012.

[14] P. Somani, A. B. Mandale, S. Radhakrishnan, "Study and development of conducting polymer-based electrochromic display devices," *Acta Mater.*, vol. 48, pp. 2859-2871, 2000.

[15] C. G. Granqvist, A. Azens, J. Isdorsson, M. Kharrazi, L. Kullman, T. Lindstrom, G. A. Niklasson, C. G. Ribbing, D. Ronnow, M. Stromme Mattson, M. Veszelei, "Towards the smart windows: progress in electromics," *J. Non-Cryst. Solids*, vol. 218, pp. 273-279, 1997.

[16] L. Zhao, L. Zhao, Y. Xu, T. Qiu, L. Zhi, G. Shi, "Polyaniline electrochromic devices with transparent graphene electrodes," *Electrochim. Acta*, vol. 55, pp. 491-497, 2009.

[17] L. Zhang, S. Xiong, J. Ma, X. Lu, "A complementary electrochromic device based on polyaniline-tethered polyhedral oligomeric silsesquioxane and tungsten oxide," *Sol. Energy Mater. Sol. Cells*, vol. 93, pp. 625-629, 2009.

[18] 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, pp. 2040-2044, 2009.

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