

## The Effect of Irradiation on the Structural, Optical and Electrical Properties of the Prussian Blue Electrochromic Thin Films

<sup>1</sup>Buthainah Abdulmunem Ibrahim, <sup>2</sup>Samir Makki and <sup>1</sup>Murtatha Jammal

<sup>1</sup>Department of Physics, College of Science, University of Diyala, Baqubah, Iraq

<sup>2</sup>Department of Physics, College of Education for Pure Science/Ibn-Al-Haitham, University of Baghdad, Baghdad, Iraq

---

**Abstract:** Prussian Blue (PB) Electrochromic (EC) thin films deposited on the FTO substrate 150, 250 and 350 nm thickness, prepared by homemade spray pyrolysis technique. Thin films were irradiated by gamma ray from Cs-137 of 0.662 MeV energy for half hour. Before and after irradiation, structural, optical and electrical properties of the electrochromic thin films were studied by X-ray diffraction, ultraviolet spectroscopy and cyclic voltammetry, respectively. After irradiation absorbance increases for (525-750) nm wavelength, furthermore, transmittance decrease for low wavelength. The voltage for coloring EC thin films decreases after irradiation as well the time of coloring and bleaching EC thin films are decreased after irradiation, also.

**Key words:** Chemical spray pyrolysis, prussian blue, electrochromic thin film, gamma radiation, wavelength, coloring and bleaching

---

### INTRODUCTION

Electrochromism which is the change of color obtained by the passage of a weak electrical current during EC substances causing chemical oxidation reactions which change the amount of light in effect which leads to change the color from transparency to opaque and vice versa (Monk *et al.*, 2015). Electrochromic materials can be classified into organic and inorganic materials as inorganic materials are readily prepared and more stable, they are used to control the amount of light and heat in smart windows which is one of the most important uses (Chen *et al.*, 2014).

Different types of materials and structures can be used in the manufacture of electrochromic devices as the transition element oxides are the most widely used in this field including tungsten oxide (WO<sub>3</sub>) which is used to manufacture intelligent glass and NiO is widely used in counting electrodes in the electrochromic equipment as well as the smart windows and other materials is poly aniline which can be formed from the chemical oxidation of ethylene when immersing electrodes in the hydrochloric acid containing a small concentration of aniline it will be a membrane on the electrode of polyethylene, depending on the case of oxidation is either light color pale yellow or yellow blackish (Wessells *et al.*, 2011).

Other types of electrochromic materials are used in technology applications, including viologen and poly oxotungstates and most commonly used in automotive plants where mirrors are manufactured using phellogen with Titanium Dioxide (TiO<sub>2</sub>) to form digital displays and it is dark blue and has a high analytical capacity comparable to the bright white of Titania and has other uses in trains and aircraft.

One of the common types of electrochromic is the prussian blue used in this research. There are several studies on the electrochromic properties of the blue barometer which began in 1978. It attracted the attention of many scientists and researchers and the thin film of the blue Prussian has a complicated formula for the relationship between electrochemistry and optical behavior due to color change with the change of voltage which can give four different colors of intensity.

**Prussian Blue (PB):** PB is inorganic electrochromic material, one of the oldest materials used in the manufacture of inorganic pigments, first produced by Diesbach in Berlin in 1704 which is very important in the production of paints and inks and the formation of pesticides and widely used in the field of medicine to rid the body of radioactive cesium used in the treatment of most cancerous diseases. PB should be considered the drug in acute thallium poisoning (Hoffman, 2003).

It has been widely manufactured for use in coating processes, printing inks and other applications of colors, without the need for an electrochemical property, the thin films of PB are used in the sensors for cholesterol and the potential for sensors to detect hydrogen peroxide in natural water (Neff, 1978; Ellis *et al.*, 1981).

There are two versions of PB which are “water insoluble (PB) ( $\text{Fe}_4(\text{Fe}^{\text{II}}(\text{CN})_6)_3$ ) and” water-soluble PB “( $\text{KFe}^{\text{III}}\text{Fe}^{\text{II}}(\text{CN})_6$ ) (Ludi and Gudel, 1973; Robin and Day, 2007). Electrochemical transformation and oxidation of PB can result in “Prussian White” (PW, Everett salt) and “Prussian Green” (PG, Berlin green), respectively.

## MATERIALS AND METHODS

### Experimental techniques

**Materials and substrates:** All chemicals are commercially, available were used without further purification. Potassium ferrocyanide ( $\text{K}_3[\text{Fe}(\text{CN})_6]$  >99%) soluble in water, iron (III) chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  >97%) soluble in water, potassium chloride ( $\text{KCl}$  >99%),  $\text{HCl}$  (ACS reagent, 37%), ethanol technical grade and deionized water of resistance  $18.2 \text{ M}\cdot \text{cm}$ , available in our lab by Millipore water purification system. FTO transparent conductor substrate ( $2.5 \times 3.0 \text{ cm}^2$ ) with sheet resistance ( $R_s = 30 \cdot /\text{cm}^2$ ).

**Preparation of spray pyrolysis samples:** The solution prepared by mixing 40 mL of (0.05 M,  $\text{K}_3[\text{Fe}(\text{CN})_6]$ ) with 40 mL of (0.05 M,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) in 100 mL beaker and stirred by magnetic stirrer for 5 min until complete dissolving. Before the deposition, the solution filtered through filter paper to remove any unresolved residual particles.

A homemade spray pyrolysis technique Fig. 1 was used for the deposition of the EC (PB) thin film on FTO substrate with thicknesses 150, 250 and 350 nm. The deposition process by spray pyrolysis technique can be divided into three main steps: the atomization of the precursor solution by the atomizer, transportation of the resultant aerosol and decomposition of the precursor on the substrate (Perednis and Gauckler, 2005).

The preparation conditions are controlled using five parameters which influence the homogeneity of the film and the adhesion to the substrate. These parameters are nozzle to substrate distance, substrate surface temperature, solution flow rate and deposition time and deposition rate. All these parameters changed until reaching to the optimum values represented in Table 1.

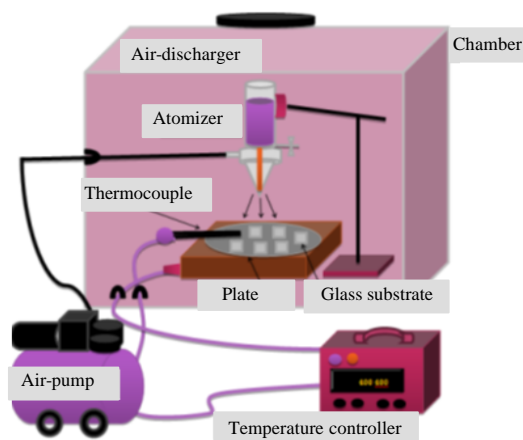


Fig. 1: Sketch of spray pyrolysis system setup

Table 1: The preparation conditions of deposit PB thin films by spray pyrolysis technique

Spray parameters	Optimum values
Nozzle height from the substrate	$40 \pm 1 \text{ cm}$
Substrate temperature	$190^\circ\text{C}$
Deposition rate	$5 \text{ mL/min}$
Deposition time	2 sec, stopped 2 min
Air pressure	$2 \times 10^5 \text{ Pa}$

**Gamma irradiation:** The radioactive source cesium-137 with energy 0.611 MeV was used. Exposure rate of irradiation is  $0.047 \mu\text{Sv}$ . The samples irradiated for half hour.

**Characterizations:** The structure of the prepared PB films was investigated at ambient temperature using X-ray technique. The XRD patterns of the prepared thin films are collected by a computer controlled X-ray diffractometer (Philips X'pert MPD) equipped with a Cu target and  $\text{CuK}$ , radiation of  $\lambda = 0.15418 \text{ nm}$  and operated at 40 kV and current 30 mA. The scanning range was from  $2\theta = 5$  to  $90^\circ$  with a step size of  $0.05^\circ (2\theta)$  and counting time of 5 s per step for the entire  $2\theta$  range.

The UV-visible spectroscopy supplied by the Shimadzu Japanese Company is used for measurements which is a two-beam type. For optical measurements, two glass bases must be placed, one at the reference window and the other at the source window. The glass base is replaced by prepared PB thin films (150, 250, 350 nm) thickness for visual measurements of the range (300-900 nm) to measure absorbance and transmittance of each thin films.

Electrochemical behavior was studied by using cyclic voltammetry, three electrodes were used in this research, prepared thin film  $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$  on FTO substrate is the working electrode,  $\text{Ag/AgCl}$  is reference electrode and the platinum wire is the counter electrode. The experiment was

carried out with the electrolyte of 0.1 M KCl solution. The measurements performed at a scanning rate 50 mV/sec and the applied potentials were from -0.5 to +0.7 V. Thin film thicknesses were determined using the electronic balance is Mettler AE-160 and its sensitivity ( $10^{-4}$ g).

**RESULTS AND DISCUSSION**

**Structural properties:** The patterns of X-ray diffraction for all thin films before and after gamma irradiation illustrated in Fig. 2 and there are diffraction peaks corresponding to levels 100, 200 and 222. The results of the structural tests showed that PB thin films before and after irradiation are a polycrystalline and cubic type.

**Optical properties:** Optical transmittance spectra of thin films are measured in the wavelength range (300-900 nm) as shown in Fig. 3 which explains the relation between transmittance and wavelength before and after irradiation. The behavior of the two figures has not changed but the transmittance has been observed to decrease as the thickness of the thin films increases. The maximum transmittance is at 450 nm wavelength while it is reduced after irradiation in this area. The lowest transmittance is in the range of 650-720 nm (in the orangeregion of the visible spectrum) (Mortimer *et al.*, 2015; Nouri, 2017).

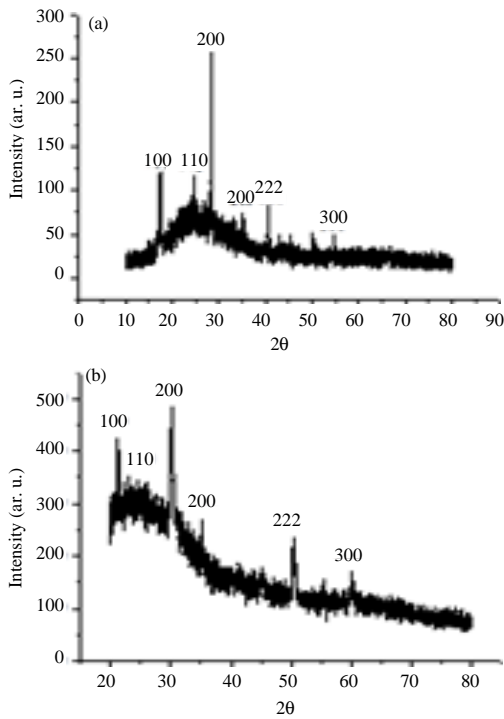


Fig. 2: X-ray diffraction for PB thin film: a) Before irradiation and b) After irradiation

Figure 4 shows the absorbance as a function of the photon wavelengths (300-900 nm) before and after gamma irradiation. It becomes clear that absorption for 150, 250 and 350 nm PB thin films before and after irradiation behaves similarly while absorption at long wavelengths greater than 550 nm increases until it reaches its highest peak at 650-750 nm. After irradiation, absorption was increased for all PB film thicknesses at wavelengths 650-750 nm.

**Cyclic Voltammetry (CV):** This technique was carried out to investigate the electrochemical properties of Fe<sub>4</sub>(Fe(CN)<sub>6</sub>)<sub>3</sub> thin films before and after gamma irradiation it was performed for six cycles and the ranges of voltage from -0.7-1 V.

Figure 5 shows the same shape PB thin films of 250 nm thickness before and after irradiation. There are two peaks, the bottom is oxidation where the first summit change the color of the thin films of cyanide iron from a colorless to blue and the second summit is the lowest the color of the PB film changes from blue to bluish green. The first bottom represents the disappearance of the green color and the return of the blue color to reappear.

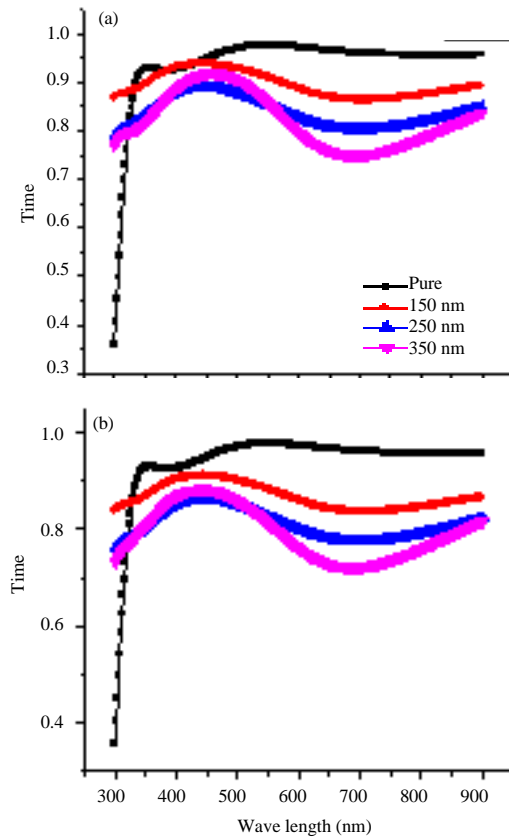


Fig. 3: Transmittance versus photon wave length: a) Before irradiation and b) After irradiation

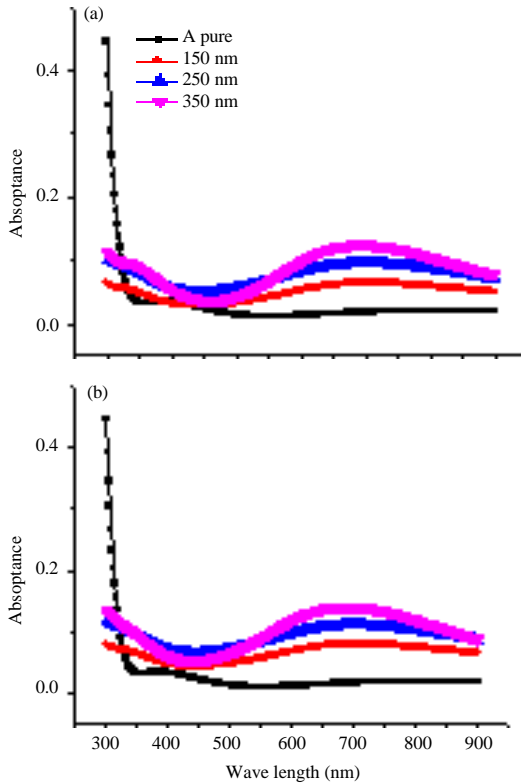


Fig. 4: Absorption versus photon wave length: a) Before irradiation and b) After irradiation

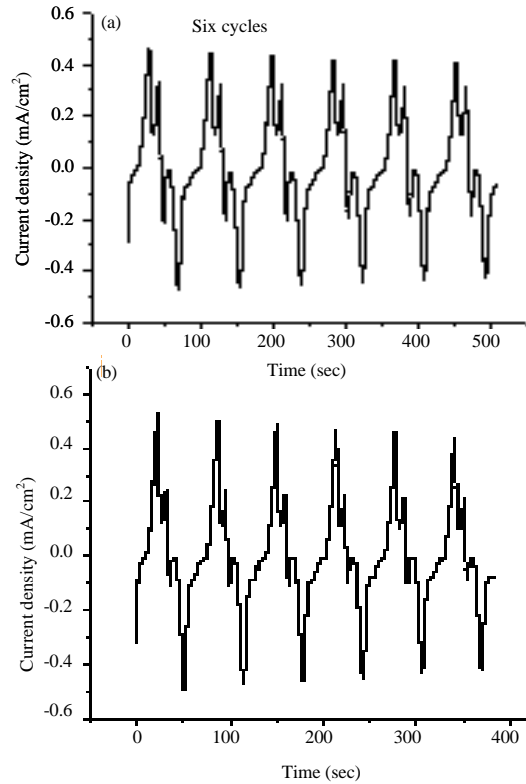


Fig. 6: Current density versus time: a) Before irradiation and b) After irradiation

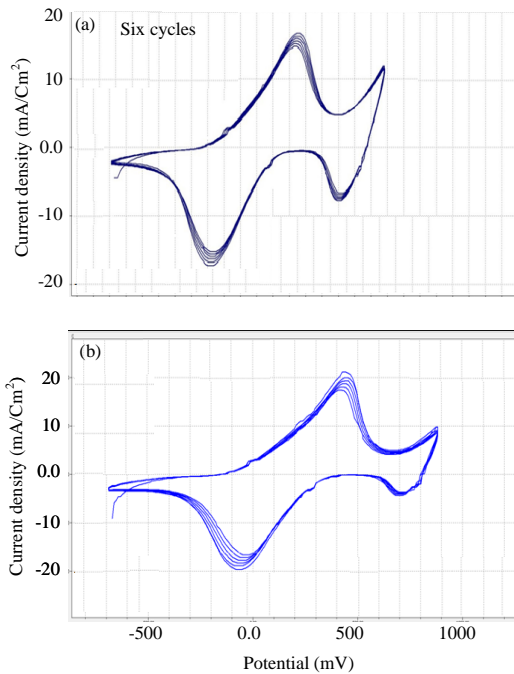


Fig. 5: Cyclic voltammety of PB thin film: a) Before irradiation and b) After irradiation

The second bottom represents the point of disappearance of the blue color, so, the film becomes a colorless transparent membrane (Najafisayar and Bahrololoom, 2013).

It is clear that gamma irradiation has caused decrease the voltage at which transition from blue color to white color (PB• PW) as well as, decreasing the voltage for which the transition from blue to green (PB• PG). The reason for this change is that the gamma irradiation caused releasing electrons during interaction with (Fe<sub>4</sub> [Fe(CN)<sub>6</sub>]<sub>3</sub>) film leading to reduce the voltage for the transition from blue to white (colorless) (PB• PW)

Figure 6 shows graphs between current density and time for 250 nm PB film thickness before and after gamma irradiation, there is a decrease of bleaching time to forming PW after irradiation whereas the coloring times are 28 and 22 sec before and after irradiation, respectively while bleaching time are 69 and 51 before and after irradiation, respectively.

### CONCLUSION

- Transmittance decrease after gamma irradiation for low wavelength

- Increase absorbance after gamma radiation at a wavelength ranges (525-750 nm). Probably may made PB films suitable for storing energy and self-provided electricity
- Voltage for coloring thin films decrease after gamma irradiation as well the coloring and bleaching time have been reduced after gamma irradiation

#### REFERENCES

- Chen, X., H. Lin, J. Deng, Y. Zhang and X. Sun *et al.*, 2014. Electrochromic fiber-shaped supercapacitors. *Adv. Mater.*, 26: 8126-8132.
- Ellis, D., M. Eckhoff and V.D. Neff, 1981. Electrochromism in the mixed-valence hexacyanides. 1. Voltammetric and spectral studies of the oxidation and reduction of thin films of Prussian blue. *J. Phys. Chem.*, 85: 1225-1231.
- Hoffman, R.S., 2003. Thallium toxicity and the role of Prussian blue in therapy. *Toxicol. Rev.*, 22: 29-40.
- Ludi, A. and H.U. Gudel, 1973. Structural Chemistry of Polynuclear Transition Metal Cyanides. In: *Inorganic Chemistry*, Ludi, A. and H.U. Gudel (Eds.). Springer, Berlin, Germany, ISBN:978-3-540-06162-5, pp: 1-21.
- Monk, P., D.R. Rosseinsky and R.J. Mortimer, 2015. Electrochromic Materials and Devices Based on Viologens. In: *Electrochromic Materials and Devices*, Mortimer, R.J., D.R. Rosseinsky and P.M.S. Monk (Eds.). Wiley-VCH, Weinheim, Germany, ISBN: 978-3-527-33610-4, pp: 57-90.
- Monk, P., R. Mortimer and D. Rosseinsky, 2007. *Electrochromism and Electrochromic Devices*. Cambridge University Press, Cambridge, England, UK., ISBN:978-0-521-82269-5, Pages: 452.
- Najafisayar, P. and M.E. Bahrololoom, 2013. Pulse electrode position of Prussian Blue thin films. *Thin Solid Films*, 542: 45-51.
- Neff, V.D., 1978. Electrochemical oxidation and reduction of thin films of Prussian Blue. *J. Electrochem. Soc.*, 125: 886-887.
- Nouri, A.S., 2017. Study of the effect of gamma radiation on some physical properties of chemically thin cadmium oxide membranes. Master Thesis, Diyala University, Baqubah, Iraq.
- Perednis, D. and L.J. Gauckler, 2005. Thin film deposition using spray pyrolysis. *J. Electroceramics*, 14: 103-111.
- Robin, M.B. and P. Day, 2007. Mixed Valence Chemistry-A Survey and Classification. In: *Molecules into Materials: Case Studies in Materials Chemistry-Mixed Valency, Magnetism and Superconductivity*, Day, P. (Ed.). World Scientific, Singapore, ISBN-13:978-981-270-038-4, pp: 142-317.
- Wessells, C.D., S.V. Peddada, M.T. McDowell, R.A. Huggins and Y. Cui, 2011. The effect of insertion species on nanostructured open framework hexacyanoferrate battery electrodes. *J. Electrochem. Soc.*, 159: A98-A103.