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THE EFFECT OF BETA PARTICLES IRRADIATION ON PHYSICAL PROPERTIES OF THE PRUSSIAN BLUE ELECTROCHROMIC THIN FILMS

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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 beta particles having energy 0.549 MeV from Sr-90 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, Cyclic voltammetry and Chronoamperometry traces (CA) respectively. After irradiation absorbance increases for (525- 750) nm wavelength, furthermore transmittance decrease for low wavelength. The bleaching voltage of PB thin films decreases after irradiation from -75 mV to +50mV, as well the bleaching time of PB thin films decreased from 69.07s to 48.98s and coloring time decreased from 28.07 s to 20.54 s.

Keywords: chemical spray pyrolysis, Prussian blue, electrochromic thin film, Beta particles irradiation, PACS: 73, 78, 88.

1. INTRODUCTION

Electrochromism is change the 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 leads to change the color from transparency to opaque and vice versa [1].

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 [2].

Different types of materials and structures can be used in the manufacture of electrocromic devices, as the transition element oxides are the most widely used in this field, including tungsten oxide (WO_3), which is used to manufacture intelligent glass, and NiO is widely used in counting electrodes in the electrocromic 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 [3].

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 (TiO2) 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 [4].

2. 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 [5]. PB should be considered the drug in acute thallium poisoning [6].

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 [7, 8].

There are two versions of PB, which are "water insoluble (PB) (Fe_4^{III} ($Fe^{II}(CN)_6)_3$)" and water-soluble PB "($KFe^{III}Fe^{II}(CN)_6$) [9, 10]. Electrochemical transformation and oxidation of PB can result in "Prussian White" (PW, Everett salt) and "Prussian Green" (PG, Berlin green), respectively.

3. EXPERIMENTAL TECHNIQUES

3.1 Materials and substrates

All chemicals are commercially available, were used without further purification. Potassium ferrocyanide (K_3 [Fe (CN)$_6$] > 99%) soluble in water, iron (III) chloride hexahydrate ($FeCl_3.6H_2O$ > 97%) soluble in water,

potassium chloride (KCl> 99%), HCl (ACS reagent, 37%), ethanol technical grade and deionized water of resistance 18.2 MΩ cm, available in our lab by Millipore water purification system. FTO transparent conductor substrate (2.5 x 3.0 cm^2) with sheet resistance (Rsh = 30 Ω/cm^2).

3.2 Preparation of spray pyrolysis samples

The solution prepared by mixing 40 ml of (0.05 M, K_3 [$Fe(CN)_6$]) with 40 ml of (0.05 M, $FeCl_3$.$6H_2O$) in 100 ml beaker and stirred by magnetic stirrer for 5 minutes until complete dissolving. Before the deposition, the solution filtered through filter paper to remove any unresolved residual particles.

A homemade spray pyrolysis technique (Figure-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 [11].

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.

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

Spray parameters	Optimum value
Nozzle height from the substrate	40 ±1cm
Substrate temperature	190^{o}C
Deposition rate	5 ml/minute
Deposition time	2 s , stopped 2 min
Air pressure	2×10^5 Pa

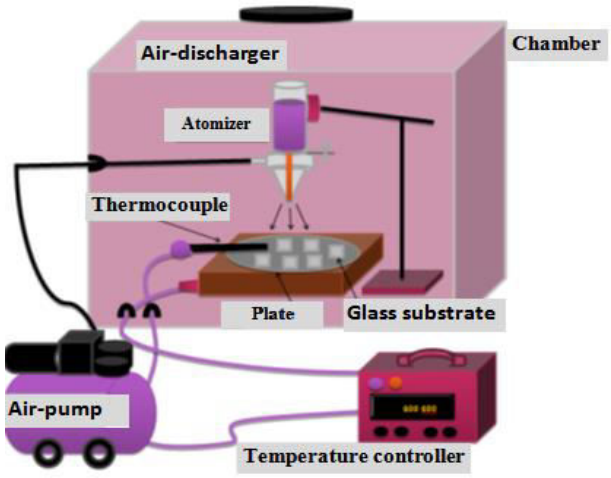

Figure-1. Sketch of spray pyrolysis system setup.

3.3 Beta particles irradiation

The radioactive source Sr-90having energy0.549 MeV is used. Exposure rate dose is0.047 μSv. The Samples irradiated for half hour.

3.4 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 CuK, radiation of λ= 0.15418 nm and operated at 40 kV and current 30 mA. The scanning range was from 2θ = 5 to 90^o with a step size of 0.05^o (2θ) and counting time of 5 s per step for the entire 2θ 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) nmthickness 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 work, prepared thin film $Fe_4(Fe(CN)_6)_3$ on FTO substrate is the working electrode, 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/s and the applied potentials were from −0.5 V to +1 V. Thin film thicknesses were determined using the electronic balance is Mettler AE-160 and its sensitivity (10^{-4}g).

4. RESULTS AND DISCUSSIONS

4.1 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.

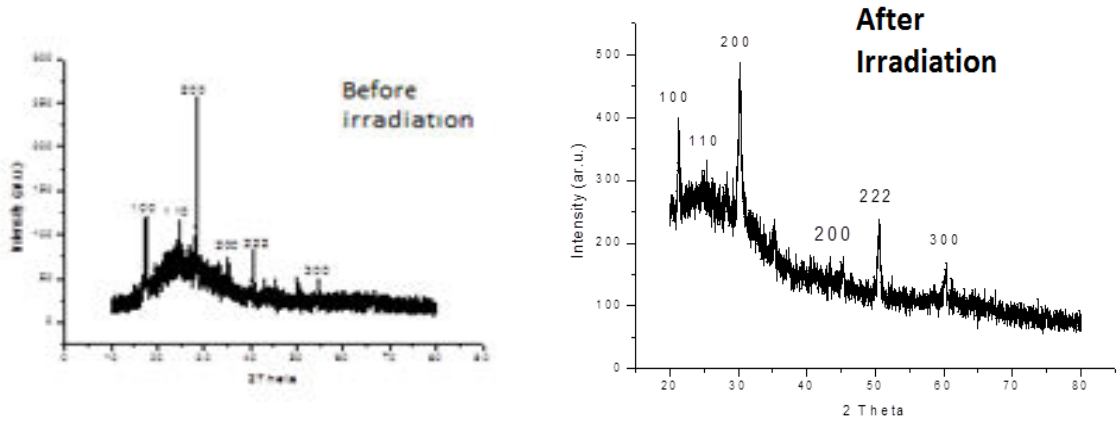

Figure-2. X-ray diffraction for PB thin film before and after irradiation.

4.2 Optical properties

Optical transmittance spectra of thin films are measured in the wavelength range (300-900) nm as shown in Figure-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 orange region of the visible spectrum) [12, 13].

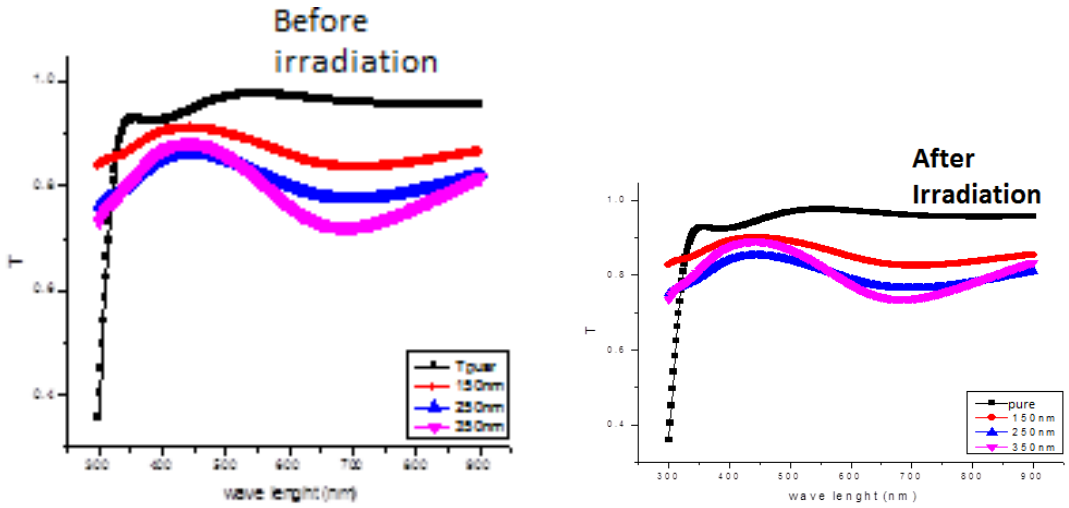

Figure-3. Transmittance versus photon wave length before and after irradiation.

Figure-4 shows the absorbance as a function of the photon wavelengths (300-900) nm before and after Betaparticles 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.

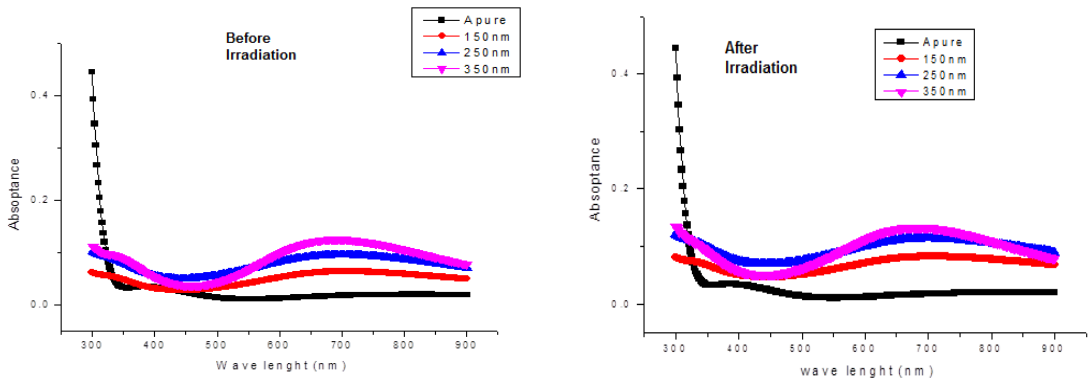

Figure-4. Absorption versus photon wave length before and after irradiation.

4.3 Cyclic Voltammetry (CV)

This technique was carried out to investigate the electrochemical properties of Fe_4 $(Fe(CN)_6]_3)$ thin films before and after gamma irradiation, it was performed for six cycles and the ranges of voltage from (- 0.7) to (1) Volts.

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. The second bottom represents the point of disappearance of the blue color, so the film becomes a colorless transparent membrane [14].

It is clear that beta irradiation has caused decrease in 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 betairradiation caused releasing electrons during interaction with $(Fe_4[Fe(CN)_6]_3)$ film leading to reduce the voltage forthe transition from blue to white (colorless)(PB→ PW). The bleaching voltage changed from -75 mV to +50 mV before and after irradiation respectively. This result indicate that the PB thin film changed from absorbed energy to provided energy, which is the promised property to become self provider energy.

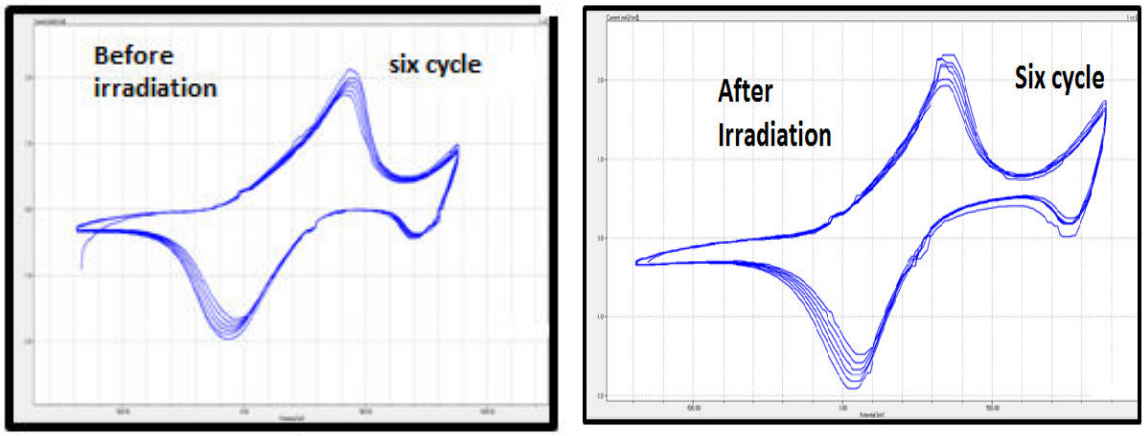

Figure-5. Cyclic voltammetry of PB thin film before and after irradiation.

Figure-6 shows graphs between current density and time for 250 nm PB film thickness before and after beta irradiation, there is a decrease of bleaching time and coloring time, whereas the coloring time changed from28.07 s to22.2 s, while bleaching time changed from 69.09 sto48.98 s before and after irradiation respectively.

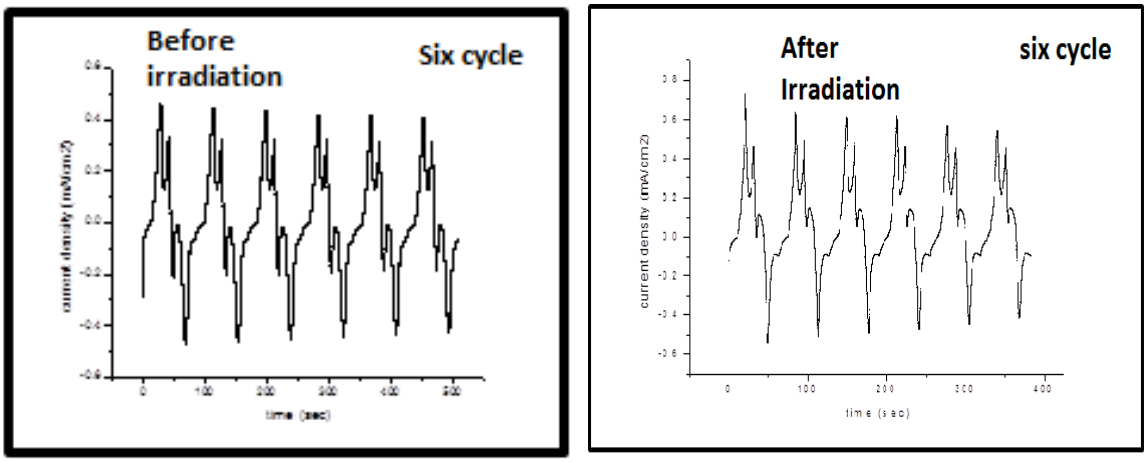

Figure-6. Current density versus time before and after irradiation.

5. CONCLUSIONS

a) Transmittance decrease after beta particles irradiation at short wavelengths.

b) Increase absorbance after beta irradiation at a wavelength ranges (525-750) nm. Probably may PB film suitable for energy storage, the film can be considered as a solar cell.

c) Bleaching Voltage of PB thin film changed from negative value to positive value after irradiation indicates that PB thin film changed from absorbed energy to provided energy; as well the bleaching time and coloring time have reduced after irradiation.

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