

# Effect of $\text{Fe}_3\text{O}_4$ on the Electro-Optic and Magneto-Electric Characteristics of (PANI/ $\text{Fe}_3\text{O}_4$ )-Ag Film

M Diantoro<sup>1,2</sup>, D Pradhana<sup>1</sup>, A A Mustikasari<sup>1</sup>, A D Kusumawati<sup>1</sup>, A Taufiq<sup>1,2</sup>, Sunaryono<sup>1,2</sup>, N Mufti<sup>1,2</sup> and H Nur<sup>3</sup>

<sup>1</sup>Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Negeri Malang (State University of Malang), Jl. Semarang No 5, Malang 65145, Indonesia

<sup>2</sup>Central Laboratory of Minerals, and Advanced Materials, Faculty of Mathematics and Natural Sciences, Universitas Negeri Malang (State University of Malang), Jl. Semarang No 5, Malang 65145, Indonesia

<sup>3</sup>Centre for Sustainable Nanomaterials, Ibnu Sina Institute for Scientific and Industrial Research Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia

Email: markus.diantoro.fmipa@um.ac.id

**Abstract.** (PANI/ $\text{Fe}_3\text{O}_4$ )-Ag films have been successfully synthesized on a glass substrate. In this study, PANI functioned as a matrix, Ag as a catalyst enhancing the conductivity of PANI, and  $\text{Fe}_3\text{O}_4$  as the influence of magnetic properties. (PANI/ $\text{Fe}_3\text{O}_4$ )-Ag was synthesized by a combination of chemical polymerization method to introduce Ag doping into PANI, and coprecipitation method of  $\text{Fe}_3\text{O}_4$ . The samples were characterized by using FTIR, X-RD, SEM, EDAX, 4-probe electrical conductivity under the employing of magnetic fields, and under the influence of light intensity. It was shown that there was a  $\text{Fe}_2\text{O}_3$  phase as the consequence of  $\text{Fe}_3\text{O}_4$  oxidized as  $\text{AgNO}_3$  protonation on the ultrasonication treatment. introducing  $\text{Fe}_3\text{O}_4$  into (PANI/ $\text{Fe}_3\text{O}_4$ )-Ag film, increase the surface density, but reduce the electrical conductivity. The increasing of magnetic field might also reduce the conductivity of (PANI/ $\text{Fe}_3\text{O}_4$ )-Ag. Further, We also obtained that the increasing of light intensity employed to the samples enhances the electrical conductivity. The electrical conductivity of (PANI/ $\text{Fe}_3\text{O}_4$ )-Ag can be tuned by controlling the  $\text{Fe}_3\text{O}_4$ , magnetic field, as well as the light intensity

**Keywords:** PANI, Ag,  $\text{Fe}_3\text{O}_4$ , microstructure, magneto-electric, electro-optic

## 1. Introduction

A research of Polyaniline (PANI) conductive polymer has become a fascinating topic recently due to its promising application potential along with a search of another natural polymer for electronics [1-2]. Many PANI related research have been focused on the application such as for gas sensor [1], the raw matrix material composition of lithium battery [2], and super-capacitor [3]. The polymer is basically as an insulator. The polymer can be modified until raising conductive characteristic through synthesis development. The synthesis method of PANI with polymerization of a chemical reaction is because it is mostly used since the synthesis is relatively simple, easy, inexpensive and efficient [4].

The effort to increase the magneto-electric on PANI composite by using PMME has been reported resulting in the highest conductivity which was  $73 \text{ Scm}^{-1}$  [5]. PANI/ $\text{Fe}_3\text{O}_4$  produced conductivity of



$10^{-9} \text{ Scm}^{-1}$  [6], while the study on an electro-optical characteristic of PANI/chlorophyll could enhance the conductivity from  $1 \text{ S/cm}$ – $8 \text{ S/cm}$  [7]. Magneto-electric is an interesting study because of the application potential on the electronic and sensor [8,9], but in the synthesis conducted, it is still challenging to get a significant and excellent material for optimizing the magneto-electric characteristic to [10]. Besides the idea of magneto-electric characteristic, the electro-optical characteristic was considered as well [11].

So far, it is rare to find the study of Ag, and  $\text{Fe}_3\text{O}_4$  doped PANI films. It is also hard to find the reports of the films primarily effect of magnetic fields and light intensity on the electrical conductivity of the films. In this work, we report on the fabrication of PANI/ $\text{Fe}_3\text{O}_4$ /Ag films and its microstructure, electrical conductivity as a function of magnetic fields, and light exposures for various  $\text{Fe}_3\text{O}_4$  dopant. It is necessary to know the correlation of electrical and magnetic characteristic of PANI. The electrical characteristic of PANI/Ag is a function of the magnetic characteristic of  $\text{Fe}_3\text{O}_4$ . Those parameters are presumably interrelated. This works also would like to infer fundamental knowledge of how to tune the electrical properties of PANI/ $\text{Fe}_3\text{O}_4$ /Ag by controlling dopant, magnetic fields, and light intensity.

## 2. Research Method

### 2.1. Instrument and Material

The instruments used in this work were Digital Scale of HF-3000 (0.019), Ultrasonic Bath LUC-405, Spin coater TC100, Furnace Brother XD-1700M, Heater and magnetic stirrer, beaker glass and Pyrex vessel (250 mL) and petri dish. The synthesis of  $\text{Fe}_3\text{O}_4$ , coprecipitation and chemistry reaction polymerization of PANI used several raw basic materials such as iron sand, aniline (PA 99.9% Merck), HCl (PA 99.9%),  $\text{NH}_4\text{OH}$  (PA 99.9%), deionized water, APS, CSA, acetone (PA 99.9%), and chloroform (PA 99.9%).

### 2.2. Procedure

**2.2.1  $\text{Fe}_3\text{O}_4$  Coprecipitation.** Firstly, the iron sand was extracted and purified by using permanent magnetic tube to get iron sand powder. The sand powder was reacted with HCl by using magnetic stirrer at a temperature of  $140^\circ\text{C}$  for 30 minutes. After that, the solution was filtered by using filter paper. The solution penetrating the filter paper was taken since  $\text{Fe}_3\text{O}_4$  dissolved in HCl. The solution then was dropped with  $\text{NH}_4\text{OH}$  gradually while being stirred for around 30 minutes until formed a black precipitate. The formed precipitated was then washed using distilled water up to pH 7 (normal pH) to get the real sample which was free from impurity. The obtained precipitate was dried on a hotplate at a temperature of  $70^\circ\text{C}$ .

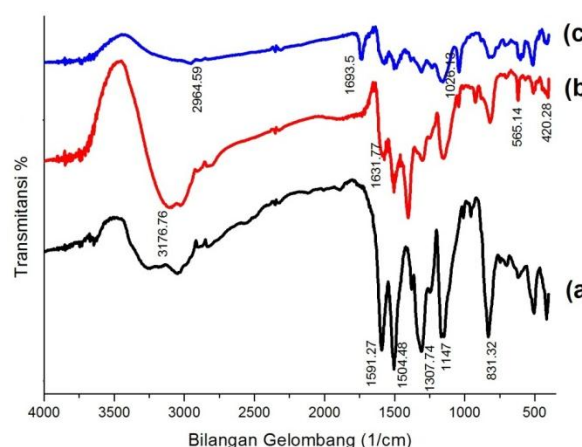
**2.2.2 PANI/ $\text{Fe}_3\text{O}_4$  Polymerization.** PANI polymerization was conducted through chemical reaction method following the method in the literature [1]. The first solution was made from aniline monomer (1.82 mL) reacted with HCl (50 mL; 0.2 M). Another solution was prepared by mixing  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  (5.71 g) with 50 mL distilled water. Both solutions were mixed and then stirred mechanically by using magnetic stirrer for 30 minutes. After stirring, the mixed solution was let precipitating for 24 hours until a green deposit was obtained. The precipitated materials were then washed with deionized water (DI water) many times until it looked like a crystal. PANI obtained from the first polymerization was PANI-ES 1 and it was then added in dropwise with  $\text{NH}_4\text{OH}$  (0.5 M; 10 mL) +  $\text{Fe}_3\text{O}_4$  of every mass variation (0.242; 0.464; 0.696; 0.928; 1.16 gram) while it was being stirred for 4 hours. These five samples are designated as 1 M, 2 M, 3 M, 4 M, and 5 M of  $\text{Fe}_3\text{O}_4$ . This deprotonation process was done at a room temperature, and it was let untreated for 24 hours to get reaction and precipitation process occurred. The obtained deposit was blue showing an emeraldine base (EB) polyaniline +  $\text{Fe}_3\text{O}_4$  (PANI-ES-2). The samples subsequently were annealed at  $80^\circ\text{C}$  for five hours for FTIR characterization.

**2.2.3 PANI/Ag/Fe<sub>3</sub>O<sub>4</sub> Protonation.** The fabrication of PANI/Ag/Fe<sub>3</sub>O<sub>4</sub> was basically followed the previous work [3] with several modifications. Firstly, introducing Ag doping was done by grinding 0.5 g of ready PANI/Fe<sub>3</sub>O<sub>4</sub> mixed with 0.5 g CSA. The mixture was ground for 15 minutes. Along with this, an AgNO<sub>3</sub> was dissolved in acetone (5 mL; 0.5 M). All prepared materials were mixed and dissolved in 10 mL chloroform for chemical reaction breaking of the atoms bonds. The sonification process was done for 45 minutes for one hour. The last step was precipitating the solution for 24 hours for protonation process. The precipitated was then filtered to obtained PANI/Ag/Fe<sub>3</sub>O<sub>4</sub> paste which will be used for XRD and FTIR characterization. The PANI/Fe<sub>3</sub>O<sub>4</sub> were similarly treated and designated as PAF1M, PAF2M, PAF3M, PAF4M, and PAF5M.

### 3. Results and Discussion

#### 3.1. Functional Groups of (PANI/Fe<sub>3</sub>O<sub>4</sub>)-Ag

Spectrum of FTIR for PANI, PANI/Fe<sub>3</sub>O<sub>4</sub>, and PANI/Ag/Fe<sub>3</sub>O<sub>4</sub> is shown in Figure 1.



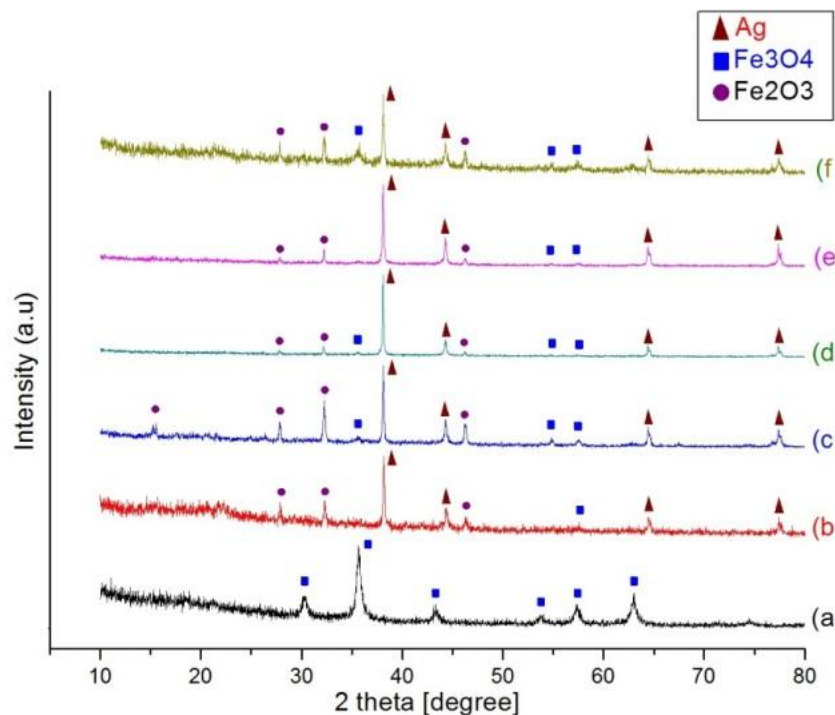
**Figure 1.** The FTIR Result of (a) PANI-EB, (b) PANI/Fe<sub>3</sub>O<sub>4</sub>; 5 M, (c) PANI/Ag/Fe<sub>3</sub>O<sub>4</sub>.

Synthesizing PANI-EB into PANI (ES II)/Fe<sub>3</sub>O<sub>4</sub> was performed by adding the mass variation of Fe<sub>3</sub>O<sub>4</sub> composite. The addition of Fe<sub>3</sub>O<sub>4</sub> caused the matrix on PANI bound and covered Fe<sub>3</sub>O<sub>4</sub> during the process of polymerization occurring. The result of FT-IR showed a functional group of PANI-EB at the wavenumber of 1591,27cm<sup>-1</sup>, 1504,48 cm<sup>-1</sup>, 1307,74 cm<sup>-1</sup>, 1147,65 cm<sup>-1</sup>, and 831,32 cm<sup>-1</sup>. This result is closely similar to our previous work [1]. The peak at 1591,27cm<sup>-1</sup> occurred due to the stretch vibration of C-N bond on quinoid ring; the peak at 1504,48 cm<sup>-1</sup> occurred due to benzoid C-N bond; the peak at 1307,74 cm<sup>-1</sup> was a stretch vibration of bipolar structure of C-N bond, the wavenumber of 1147,65 cm<sup>-1</sup> was a bending section result of aromatic C-H bond, and the wavenumber at the range of 831,32 cm<sup>-1</sup> was the consequence of aromatic C-H bond. The absorption difference of IR Fe<sub>3</sub>O<sub>4</sub> infused when PANI-ES polymerization occurred toward PANI-EB peak is shown in Figure 1 (b). From the figure, we can see that the transmittance plain was at the wave number of 3176,76 cm<sup>-1</sup>, 1631,77 cm<sup>-1</sup>, 565,14 cm<sup>-1</sup>, and 420,28 cm<sup>-1</sup>. The absorption of IR Fe<sub>3</sub>O<sub>4</sub> at 3176,76 cm<sup>-1</sup> identified the function cluster of -OH- occurring in the range of 3000-4000 cm<sup>-1</sup>, the wavenumber of 1631,77 cm<sup>-1</sup> identified function cluster of H<sub>2</sub>O, the wavenumber of 565.14 cm<sup>-1</sup> happened as a consequence of the presence of (Fe<sup>3+</sup>-O<sup>2+</sup>) and for the wavenumber of 420.28 cm<sup>-1</sup>, it was a functional group of (Fe-O). From Figure 1 (b), it was identified that Fe<sub>3</sub>O<sub>4</sub> was bound with PANI matrix during the polymerization process. When Ag added to PANI/Fe<sub>3</sub>O<sub>4</sub> it might change the origin bonds of PANI and were replaced by Ag<sup>+</sup> ion from AgNO<sub>3</sub> of which bond was broken. The identification of FTIR for Ag ion at the spectrum of 2965.15 cm<sup>-1</sup> occurred due to the presence of C-Ag bond; the wavenumber at 1693,5 cm<sup>-1</sup>

showed a functional group of  $\text{-N-H-}$  enabling  $\text{-H-}$  atom attached with  $\text{-N-}$  was replaced by Ag into  $\text{-N-Ag-}$ . While the wave number of  $1026,13\text{ cm}^{-1}$  represent a function of  $\text{-OH-}$ .

### 3.2. Crystal Structure of $(\text{PANI}/\text{Fe}_3\text{O}_4)\text{-Ag}$

The XRD diffraction patterns is provided to study the crystallinity and phase formed from PANI/Ag/Fe<sub>3</sub>O<sub>4</sub> film. The un-doped and Fe<sub>3</sub>O<sub>4</sub> doped (PANI/Fe<sub>3</sub>O<sub>4</sub>)-Ag is displayed in Figure 2.



**Figure 2.** XRD Patterns of (a). PANI/Fe<sub>3</sub>O<sub>4</sub>; 5M, (b). PAF1M, (c). PAF2M, (d). PAF3M, (e). PAF4M, and (f). PAF5M.

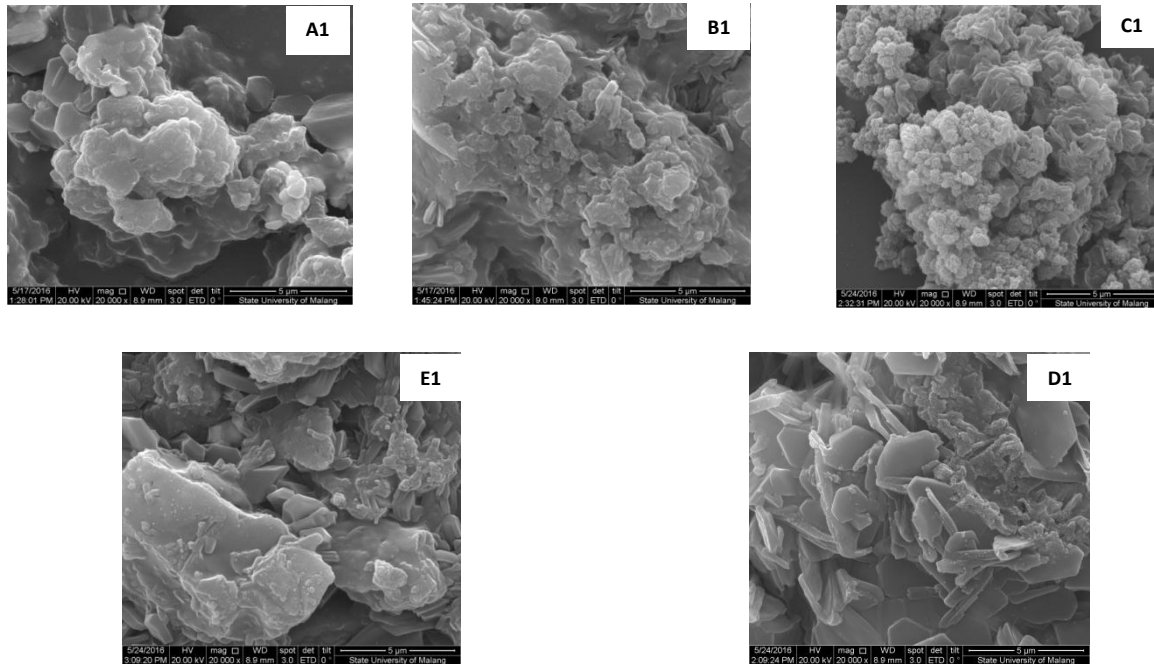
The undoped PANI/ Fe<sub>3</sub>O<sub>4</sub> sample as depicted in Figure 3.3 (a) we detect only Fe<sub>3</sub>O<sub>4</sub> peaks are appear. Introducing silver ion in the sample PAF1M give rise to the appearance of other phases of Fe<sub>2</sub>O<sub>3</sub>, and Ag. It is observed that the Bragg peak of PAF1M sample indicated at the position of  $2\theta = 57^\circ$  for Fe<sub>3</sub>O<sub>4</sub> phase. It is also detected a Fe<sub>2</sub>O<sub>3</sub> phase showing by appearing peaks position at  $2\theta$  of  $28^\circ$ ,  $32.25^\circ$ , and  $46.11^\circ$ . The remaining are the peak of Ag  $2\theta = 38,2^\circ$ ,  $44,3^\circ$ ,  $64.5^\circ$  and  $77.4^\circ$ . The peaks of For PAF2M indicating the appearance of Fe<sub>3</sub>O<sub>4</sub> which were observed at  $30$ ,  $53^\circ$ , and  $57^\circ$ . A weak peak at  $2\theta = 46.11^\circ$  assigned of Fe<sub>2</sub>O<sub>3</sub> phase. Similar to the other samples, the PAF3M, PAF4M, and PAF5M also showing the appearance of Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub>, and Ag phases.

A few parts of Fe<sub>3</sub>O<sub>4</sub> particle transformed into Fe<sub>2</sub>O<sub>3</sub> during the process introducing Ag dopant. Although the initial dopant was Fe<sub>3</sub>O<sub>4</sub> phase, from the XRD patterns, we could easily see that Fe<sub>2</sub>O<sub>3</sub> also appeared in all doped samples. It means that the Fe<sub>2</sub>O<sub>3</sub> found act as dopant phase. The partial transformed of Fe<sub>3</sub>O<sub>4</sub> into Fe<sub>2</sub>O<sub>3</sub> was caused by several factors such as the process of incorporating of Ag into PANI/Fe<sub>3</sub>O<sub>4</sub>, and also possible came from sonochemical process. In sonification step, breaking AgNO<sub>3</sub> bond may occurred and transformed Ag<sup>+</sup> and NO<sub>3</sub><sup>-</sup>. The Ag<sup>+</sup> separated from NO<sub>3</sub><sup>-</sup> might enter to PANI  $\text{-C=H-}$  bond cluster and possibly transformed into  $\text{-C=Ag-}$  and  $\text{-N-H-}$  bond cluster changed into  $\text{-N-Ag-}$ . The process of bond separation in sonification made some Fe<sub>3</sub>O<sub>4</sub> within PANI/Fe<sub>3</sub>O<sub>4</sub> were broken into Fe<sup>+</sup> and O<sup>-</sup>, so some Fe<sub>2</sub>O<sub>3</sub> phase appeared in (PANI/Fe<sub>3</sub>O<sub>4</sub>)-Ag phase. The other factor of the appearance of Fe<sub>2</sub>O<sub>3</sub> phase in PANI/Ag/Fe<sub>3</sub>O<sub>4</sub> is because of Ag<sup>+</sup> ion is too reactive to O<sub>2</sub>. Therefore, when Ag<sup>+</sup> is separated from NO<sub>3</sub><sup>-</sup>, it can be reactive to the Fe<sub>3</sub>O<sub>4</sub> particle until

it is oxidized becomes  $\text{Fe}_2\text{O}_3$ . The third factor is  $\text{Fe}_3\text{O}_4$  particle becomes reactive in nano-size, enabling such condition may happen in the process of giving Ag doping by some of  $\text{Fe}_3\text{O}_4$  oxidized becomes  $\text{Fe}_2\text{O}_3$  phase.

### 3.3. Microstructure of $(\text{PANI}/\text{Fe}_3\text{O}_4)\text{-Ag}$

The effect of  $\text{Fe}_3\text{O}_4$  to the  $(\text{PANI}/\text{Fe}_3\text{O}_4)\text{-Ag}$  film on its microstructure could be seen based on the topography surface by SEM characterization as depicted in Figure 3.



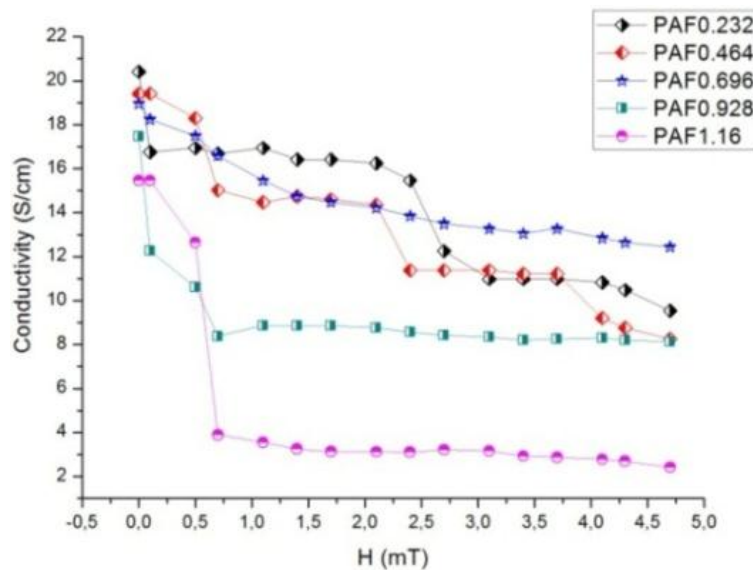
**Figure 3.** The Microstructure of (a1) PAF1M, (b1) PAF2M, (c1) PAF3M, (d1) PAF4M, (e1) PAF5M

These SEM images do not contain the same features with the metallic doped of PANI [1]. It is seen that the morphology of  $(\text{PANI}/\text{Fe}_3\text{O}_4)\text{-Ag}$  samples are plate-like. It might be due to the synthesis of PANI was by using chemical reaction polymerization. In Figure 3 (A1), the elemental content of  $\text{Fe}_3\text{O}_4$  was fewer than the other samples, so the granular microstructure of  $(\text{PANI}/\text{Fe}_3\text{O}_4)\text{-Ag}$  surface remained plate-like and smooth. The size of PANI formed was around 0.3-0.5  $\mu\text{m}$ . In Figure 3. (B1), Fe increased to represent the existing of  $\text{Fe}_3\text{O}_4$  or  $\text{Fe}_2\text{O}_3$ . The influence of  $\text{Fe}_3\text{O}_4$  affected the  $(\text{PANI}/\text{Fe}_3\text{O}_4)\text{-Ag}$  microstructure tended to rougher and covered with the cavity of granular PANI. The  $\text{Fe}_3\text{O}_4$  particle formed in  $(\text{PANI}/\text{Fe}_3\text{O}_4)\text{-Ag}$  looked cubic spinel, even the  $\text{Fe}_2\text{O}_3$  formed from  $\text{Fe}_3\text{O}_4$  oxidation had cubic spinel matched with AMCSD 0020515. Figure 3 (C1, D1, and E1) show that the influence of  $\text{Fe}_3\text{O}_4$  on PANI microstructure made the rough surface became rougher as the amount of  $\text{Fe}_3\text{O}_4$  increased.

### 3.4. Magneto-Electric of $(\text{PANI}/\text{Fe}_3\text{O}_4)\text{-Ag}$ by Using 4 Probes

The magneto-electric characteristic of  $(\text{PANI}/\text{Fe}_3\text{O}_4)\text{-Ag}$  film is an interesting complement study in which the  $\text{Fe}_3\text{O}_4$  has a magnetic characteristic as the PANI of which conductivity is increased by giving Ag doping.



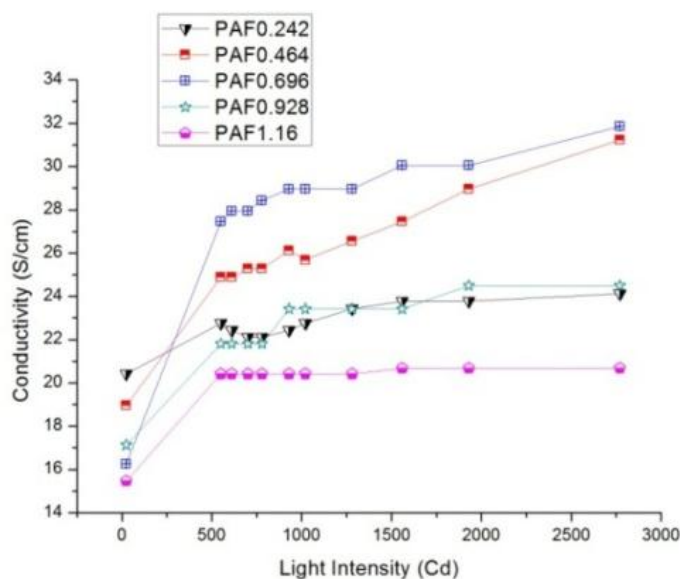


**Figure 4.** Conductivity as a function of Magnetic Field of (PANI/Fe<sub>3</sub>O<sub>4</sub>)-Ag Samples

It is observed in Figure 4, that employing magnetic field resulting to reduce electrical conductivity for all ranges of Fe<sub>3</sub>O<sub>4</sub> doping. This feature is similar to the pure extracted PANI as reported by other work [8]. Another group, reported that at low magnetic field, electrical conductivity is obviously increased by increase of magnetic field. [16]. When the more Fe<sub>3</sub>O<sub>4</sub> compound was added to PANI/Ag/Fe<sub>3</sub>O<sub>4</sub>, the conductivity is getting reduced. In general also observed that the magnetic field affected to decrease the electrical conductivity. Interesting phenomena achieved in this figure, both increased of Fe<sub>3</sub>O<sub>4</sub> dopant as well as increase of magnetic intensity give rise to reduced the electrical conductivity. It means that, we can control electrical conductivity of PANI/Ag/Fe<sub>3</sub>O<sub>4</sub> films by controlling Fe<sub>3</sub>O<sub>4</sub> dopant and or employed external magnetic field. The magnetic field applied to the (PANI/Fe<sub>3</sub>O<sub>4</sub>)-Ag material made the magnetic dipoles of inactive Fe<sub>3</sub>O<sub>4</sub> became magnetized by external magnetic field (H) applied. The magnetic dipole influenced by magnetic field made the electron dissipation brought the charge on the PANI bond chain or from ferrites compounds. The dissipation disturbed the electron path in the PANI bond chain, so the electron became harder to move to deliver the electric charge since it was quantized by the magnet dipole of Fe<sub>3</sub>O<sub>4</sub>.

### 3.5. Electro-Optic Characteristics of (PANI/Fe<sub>3</sub>O<sub>4</sub>)-Ag Film by Using 4 Probes

The electric-optic characteristic of (PANI/Fe<sub>3</sub>O<sub>4</sub>)-Ag sample is an influence of light intensity on the conductivity. Inducing doping of Fe<sub>3</sub>O<sub>4</sub> as well as the light intensity significantly change the electrical conductivity of (PANI/Fe<sub>3</sub>O<sub>4</sub>)-Ag. The light intensity applied on (PANI/Fe<sub>3</sub>O<sub>4</sub>)-Ag made the electrical conductivity of material increased. It is presumably that the intensity caused thermal energy causing electron energy increased in the PANI bond chain within the valence band. Such condition made the electron easily moved to the conduction band. The band energy from the sample could be derived by giving light intensity in the range in which quantum energy  $h\nu$  should exceed the band energy. The light intensity applied on (PANI/Fe<sub>3</sub>O<sub>4</sub>)-Ag sample was about 550 to 2770 Lux. This feature may be similar to the thermal applied to PANI which also increase as the temperature increase [16]. It is revealed that the effect of light intensity below 550 Lux did not affected to the (PANI/Fe<sub>3</sub>O<sub>4</sub>)-Ag conductivity. There is no step-like patterns of intensity induced of electrical conductivity as in borosilicate glass [17].



**Figure 5.** The Graph of Correlation Between Light Intensity and Conductivity of PAF1M; PAF2M; PAF3M; PAF4M; and PAA5M

#### 4. Conclusion

Based on the characterization of microstructure by using SEM, the bigger the addition of  $\text{Fe}_3\text{O}_4$ , the density of (PANI/ $\text{Fe}_3\text{O}_4$ )-Ag film increases as well. The increase of surface density also induces to the reduce of electrical conductivity. This implies that introducing  $\text{Fe}_3\text{O}_4$  into (PANI/ $\text{Fe}_3\text{O}_4$ )-Ag film, is not in line with the increase in surface density. The response of increasing of magnetic field might also reduce the conductivity of (PANI/ $\text{Fe}_3\text{O}_4$ )-Ag film. Further, we also obtained that the increasing of light intensity employed to the samples enhances the electrical conductivity. The electrical conductivity of (PANI/ $\text{Fe}_3\text{O}_4$ )-Ag can be tuned by controlling the  $\text{Fe}_3\text{O}_4$ , magnetic field, as well as the light intensity.

#### 5. References

- [1] Fratoddi I, Venditti I, Cametti C and Russo M V 2015 Chemiresistive polyaniline-based gas sensors: A mini review *Sens. Actuators B Chem.* **220** 534–48
- [2] Wang D, Wang X, Yang X, Yu R, Ge L and Shu H 2015 Polyaniline modification and performance enhancement of lithium-rich cathode material based on layered-spinel hybrid structure *J. Power Sources* **293** 89–94
- [3] Kim J, Ju H, Inamdar A I, Jo Y, Han J, Kim H and Im H 2014 Synthesis and enhanced electrochemical supercapacitor properties of Ag– $\text{MnO}_2$ –polyaniline nanocomposite electrodes *Energy* **70** 473–7
- [4] Ghaffari-Moghaddam M and Eslahi H 2014 Synthesis, characterization and antibacterial properties of a novel nanocomposite based on polyaniline/polyvinyl alcohol/Ag *Arab. J. Chem.* **7** 846–55
- [5] Angappane S, Srinivasan D, Rangarajan G, Prasad V, Subramayam S . and Wessling B 2000 Transport and magneto-transport study on some conducting polyanilines *Phys. B* 284–8
- [6] Beata Z, Patrycja A, Petr J, Petrovsky E, Pavel B and Danniell H 2016 Magnetoconductive maghemite core/polyaniline shell nanoparticles: Physico-chemical and biological assessment *Colloids Surf. B Biointerfaces*

- [7] Manna J S, Basu S, Mitra M K, Mukherjee S and Das G C 2012 Evolution of chlorophyll/polyaniline nanorod network with enhanced electro-optic property *Mater. Lett.* **76** 147–50
- [8] Saha J, Sharma G, Kaushik S D, Rani V, Sudesh, Siruguri V and Patnaik S 2016 Magneto-electric coupling in  $\text{Ca}_3\text{CoMnO}_6$  thin films *Proc. 20th Int. Conf. Magn. Barc. 5-10 July 2015* **400** 282–5
- [9] Tripathy S N, Mishra B G, Shirolkar M M, Sen S, Das S R, Janes D B and Pradhan D K 2013 Structural, microstructural and magneto-electric properties of single-phase  $\text{BiFeO}_3$  nanoceramics prepared by auto-combustion method *Mater. Chem. Phys.* **141** 423–31
- [10] Zhou L, Fu Q, Zhou D, Xue F, Tian Y and Hao L 2015 Magneto-electric coupling study in multiferroic  $\text{La}_{0.7}\text{Ba}_{0.3}\text{MnO}_3\text{--BaTiO}_3$  composite ceramic at room temperature *Ceram. Int.* **41** 2367–72
- [11] Wu J, Wang W, Wang L, Liu J, Chen K and Bo S 2016 Introduction of fluorine to change the dielectric environment of nonlinear optical chromophores for improved electro-optic activities *Mater. Lett.* **164** 636–9