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Analysis of XRD Characterization of Fe_3O_4/Polypyrrole Nanocomposite Prepared by Sol-Gel Method

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ABSTRACT

Nanocomposites can be thought of as solid structures with nanometer-scale dimensions that repeat at the distances between different structural constituents. In this study, Fe_3O_4 was used as a filler and Polypyrrole polymer as the matrix material. This research was conducted by varying the Fe_3O_4: Polypyrrole composition of 5 variations including 30%, 40%, 50%, 60%, and 70% w/w. This research was conducted to analyze the results of the XRD characterization of Fe3O4/Polypyrrole nanocomposite using the sol-gel method. The tool used in this research is X-Ray Diffraction (XRD) obtained the phase structure, crystal size, and microstrain. Based on the results of the study, the greater the polypyrrole composition, the greater the crystal size and microstrain. Details of the results are described in this paper.

Keywords : *Nanocomposite, Polypyrrole, sol-gel, XRD, magnetite*

I. INTRODUCTION

Iron sand is a sand deposit containing iron particles (magnetite), which are located along the coast, formed due to surface water, weathering, and waves against the original rock containing iron minerals such as iron oxide, ilmenite, magnetite, then accumulates and is washed away by sea waves. Magnetic nanoparticles can be applied in various fields and have varied physical properties. One example of magnetic particles that can be made in nanometer size is iron oxides such as Fe_3O_4 (magnetite) [1].

In terms of crystal structure, Fe_3O_4 nanoparticles have an inverse spinel cubic crystal structure. The molecular formula of Fe_3O_4 can be written as $(Fe_{2+})(Fe_{3+})_2O_4$. Based on Figure 1, there are 8 trivalent Fe_{3+} cations occupying the tetrahedral site, 8 Fe_{3+} cations also occupying the octahedral site, and 8 divalent Fe_{2+} cations occupying the octahedral site. Fe_{3+} cations occupying tetrahedral and octahedral sites have the same magnitude of resultant magnetic moment, but opposite orientations .

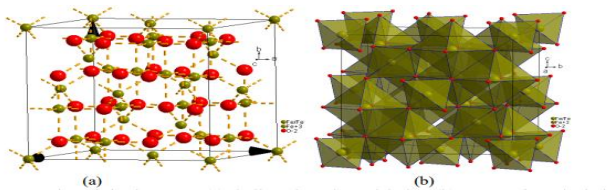


Fig. 1. Fe_3O_4 crystal structure: (a) ball and stick model and (b) tetrahedral and octahedral geometries for the inverse spinel structure [2].

The iron rock consists of iron oxide minerals such as hematite (Fe_2O_3), maghemite (Fe_2O_4), and magnetite (Fe_3O_4). Magnetite (Fe_3O_4) is a mixture of iron oxide which is formed due to the reaction of iron(II) oxide with iron(III) in which the resulting results are superior to iron(II) oxide and iron(III) oxide respectively.[3]. Magnetite (Fe3O4) is an iron oxide which has the strongest magnetic properties compared to other iron oxides and is the most commonly found [3]. Magnetite (Fe3O4) is one of the iron oxide group minerals which has the strongest magnetic properties in nature with a cubic crystal structure. Changes in the particle size of magnetite (Fe3O4) will affect its properties [1]

A conductive polymer is a material that can conduct electric currents. Conductive polymers have advantages such as absorbing electromagnetic waves when compared to other metals and being able to reduce reflections . The types of conductive polymers include Polyaniline (PAni), Polyethylene terephthalate (PET), and Polypyrrole (PPy). Polypyrrole (PPy) is the most widely used conductive polymer in research because it has high electrical conductivity, good chemical stability in the air, and is easy to synthesize [4]. One of the most widely used polymer types in research is Polypyrrole (PPy). Polypyrrole (Ppy) is used in various potential applications such as gas sensors, biosensors, cables, capacitors, anti-electrical coatings, polymer batteries, anti-electrostatic coatings, microactuators, biomedical, electronic devices, and others [5]

In the field of nanocomposite technology, it has several applications, including as a battery, fuel, and supercapacitor material. Supercapacitors are energy storage devices that have been widely applied in electronics and transportation. Supercapacitors have several advantages, namely, they do not require a maintenance process, have a long lifetime, can fast charge and discharge processes, and can operate effectively in a variety of environmental conditions [6].

In the manufacture of nanocomposites, several methods are used, one of which is the spin coating method and the sol-gel method. In this study, the sol-gel method was used for the manufacture of nanocomposites. The sol-gel method is a method for making nano-sized particles, the sol-gel method in the process uses a wet technique because the process it goes through involves a solution as the medium [7]. The sol-gel method has advantages over other methods, namely to produce a material whose composition can be controlled and a high degree of homogeneity [8].

Research on nanocomposite coatings has been carried out by many researchers. As has been studied regarding the microstructure and magnetic properties of Fe_3O_4/PVDV nanocomposite thin films. Based on this research, it was found that as the Fe_3O_4 composition increases, the crystal size decreases, and the grain engraving increases [9].

In this article, researchers conducted research on Polypyrrole (PPy) polymer nanocomposites synthesized by the sol-gel method. To see the resulting Fe_3O_4/Polypyrrole nanocomposite, the researchers varied the composition of Fe_3O_4:Polypyrrole used. To view the crystal structure, crystal size, microstrain, and X-Ray diffraction (XRD) characterization tools are used. The benefit of this research is to increase the storage capacity and conductivity of the supercapacitor material according to research [6] a good supercapacitor must have a large surface area and a crystal size in the order of nanometers.

II. METHOD

The type of research used is experimental research, research that examines the analysis of the microstructure properties of Fe_3O_4/polypyrrole nanocomposites synthesized by the Sol-Gel Method. The research was conducted from March to June 2022 at the Material Physics and Biophysics Laboratory of the Physics Department and the Chemistry Laboratory of the State University of Padang. X-Ray Diffraction (XRD) is used to obtain particle size and identify a crystalline phase in the material by determining the lattice structure parameters. The higher the intensity value, the larger the grain size obtained [10]. XRD technique is used to obtain particle size and identify the crystalline phase in a material by determining the lattice structure parameters. The material analyzed by the XRD technique is fine soil, homogenized, and the average bulk composition is determined [11]. The results of measurements using XRD are in the form of diffractograms and the structure and quality of the crystals being tested can be known. The crystal structure can be analyzed using Bragg diffraction.

The research was carried out in several stages, namely, synthesizing Fe_3O_4 from iron sand, making Fe_3O_4 precursors, making Fe_3O_4/polypyrrole nanocomposites, and conducting microstructure analysis of Fe_3O_4 and data processing techniques. The research steps can be seen in the form of a flow chart in Figure 2 below, namely:

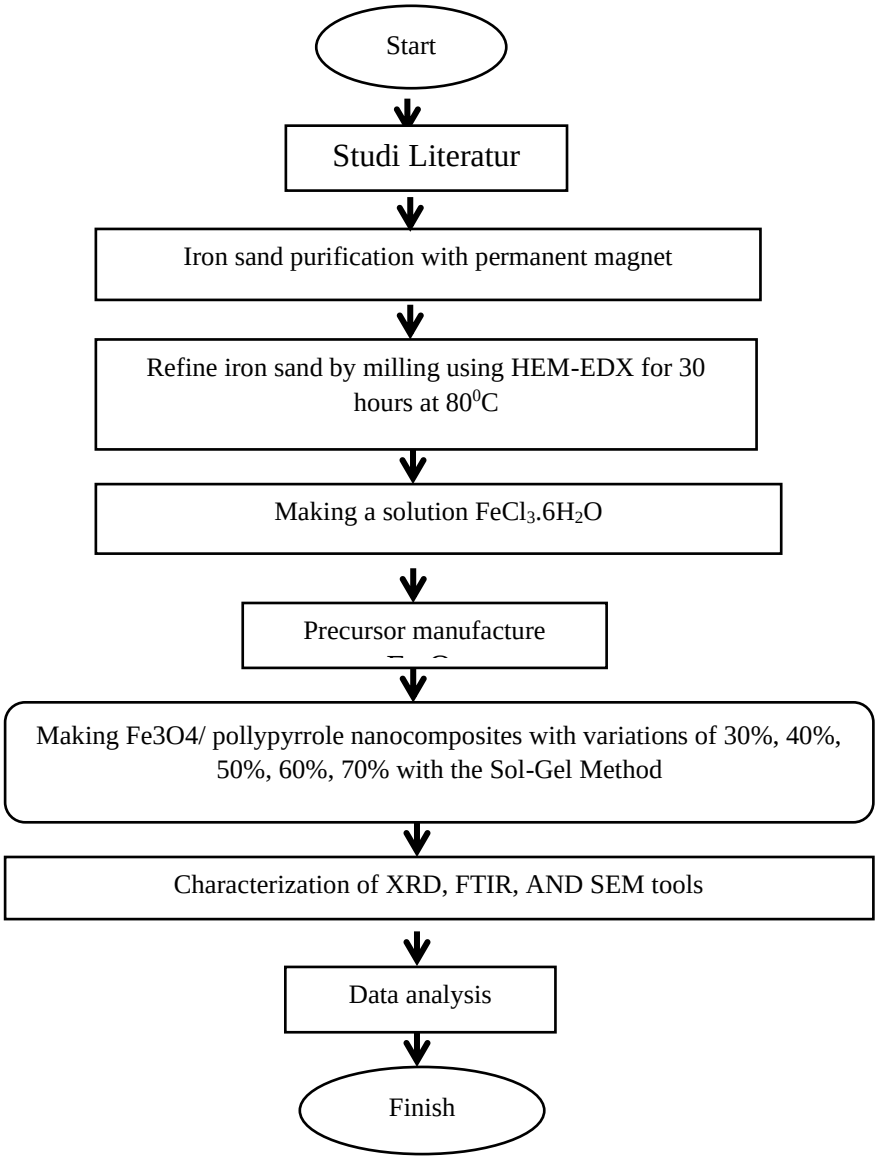


Fig.2. Flowchart

As shown in Figure 2, in the literature study, namely the introduction of materials or tools that will be used during the research. The tools used in this research are HEM-E3D, magnetic stirrer, digital scale, measuring cup, evaporating dish, and thermometer. The materials used are distilled water, aquabidest, tapioca flour, n-hexane, ethanol, oleic acid, ethylene glycol, NaOH, and polypyrrole. The characterization tool used is X-Ray Diffraction (XRD). To get the crystal size value from the XRD results, the Scherer. equation is used.

The refining process using HEM-E3D is carried out using a ratio of milling balls to samples, namely 1:10, where the number of samples needed in one milling time is 6 grams and the weight of the milling ball is 60 grams. The milling process is carried out for 30 hours. At 30 hours of milling, the hematite phase was lost, so only one phase was left, namely Fe2O4. This is because the high-energy milling process can improve the reaction kinetics associated with the formation of magnetite and hematite [12].

The stage of making the precursor of Fe_3O_4 using $FeCl_3.\ _6H_2O$ was carried out at room temperature by reacting Fe_3O_4 and hydrochloric acid (HCL used at a concentration of 35%) (1g of magnetite required 2 mL of hydrochloric acid). After all the reactions took place, then the ferric chloride solution was separated from the remaining iron sand precipitate. Next, the magnetite sol-gel process was carried out.

The magnetite sol-gel synthesis process starts from several steps, namely, the first step is to dissolve 2.1 grams of $FeCl_3.\ _6H_2O$ into 12 ml Aquabidest. Then the solution was stirred using a magnetic stirrer at room temperature at a constant speed. The second step was adding 18 ml of n-hexane to the solution until two separate layers were seen on the surface of the solution. The next step is to put NaOH and 20 ml of ethanol into the solution. Then heat the solution on a hot plate at a temperature of 500oC for 6 hours, heating is carried out to produce a layer of iron oxide sol. The last step in the sol-gel synthesis is to slowly drip oleic acid onto the stirred sol at 500oC, then let the sol sit for 48 hours at room temperature.

In the manufacture of Fe_3O_4/PPy Sol-Gel, Fe_3O_4 nanocomposite dissolved in 300 ml of aquabidest and stirred using a magnetic stirrer for 1 hour, then add pyrrole little by little into the solution with a concentration ratio of 30%, 40%, 50%, 60% Fe_3O_4/PPy. and 70%. Add $FeCl_3$ and stir using a magnetic stirrer at a temperature of 0-500C for 8 hours, then wash the solution using aquabidest and ethanol, then dry in the oven at 600C for 24 hours.

Fe_3O_4/Polypyrrole nanocomposite samples with variations of 30%, 40%, 50%, 60%, and 70% were characterized using XRD to determine the phase, crystal structure, and crystal grain size.

$$D = \frac{K\ \lambda}{\beta \operatorname{Cos} \theta} \qquad (1)$$

D = crystal size (nm)

k = constant (0.9)

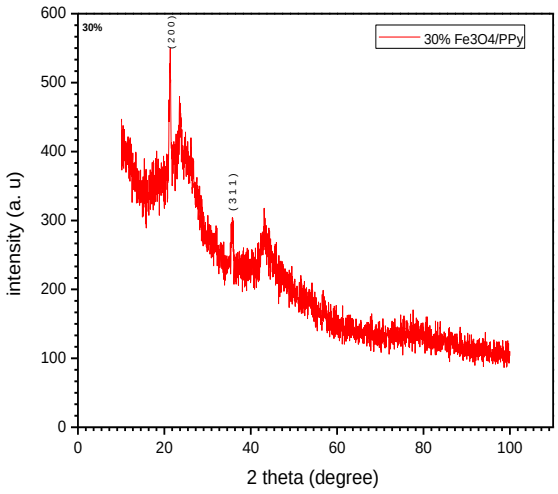
λ = Cu wavelength (0.15406 nm)

β = FWHM (rad)

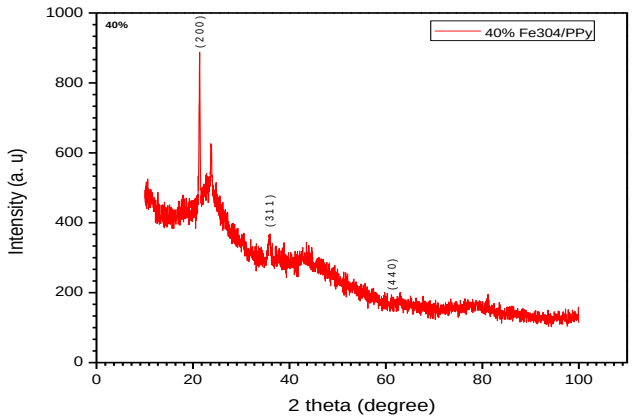
θ = Diffraction angle [13]

III. RESULTS AND DISCUSSION

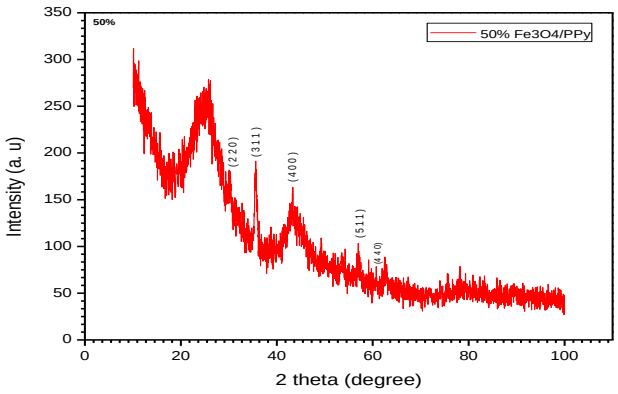
The results of the Fe_3O_4/polypyrrole nanocomposite research were tested using an XRD tool, namely crystal structure, and crystal size, as shown in Figure 3,



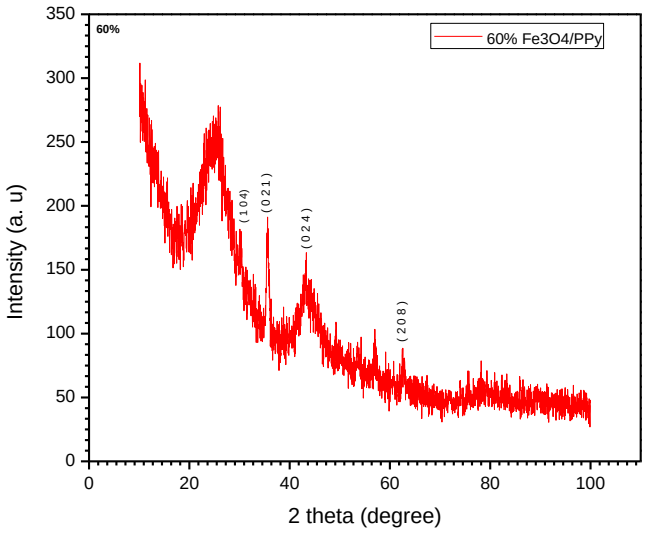
(a)


40%
40% Fe304/PPy
(200)
(311)
(440)
Intensity (a. u)
2 theta (degree)

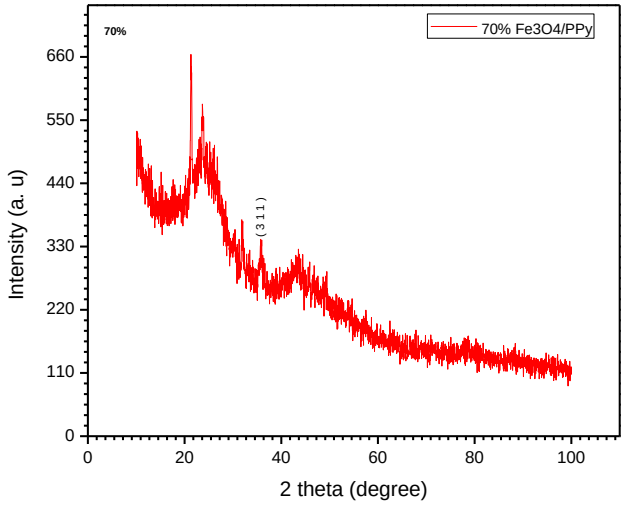
(b)


50%
50% Fe3O4/PPy
(220)
(311)
(400)
(511)
(440)
Intensity (a. u)
2 theta (degree)

(c)


60%
60% Fe3O4/PPy
(104)
(021)
(024)
(208)
Intensity (a. u)
2 theta (degree)

(d)



(e)

Fig. 3. X-ray diffraction pattern and emergent phase of Fe_3O_4/Polypyrrole

Figure 3 shows the diffraction pattern of Fe_3O_4/Polypyrrole nanocomposite with composition variations of 30%, 40%, 50%, 60%, and 70% in the form of powder. The results of the x-ray test above show that there is a change in intensity in certain plane orientations due to the effect of adding Fe_3O_4/Polypyrrole composition. Changes in the intensity value can be seen from the processing results using HighScorePlus Software. Based On Figure 3, the bes composition of 30%, 40%, 50%, and 70%.

3.1 Crystal structure, and crystal size

Table 1. The pattern of each peak intensity and angle of 2 θ composition variation of 30%,

Angel 2θ (º)	**h k l**	**FWHM**	**Intensity (a.u)**	**Crystal structure**
21.337	2 0 0	0,307	49.0	*Cubic*
35.7591	3 1 1	0,4093	43.2	*Cubic*

Table 2. The pattern of each peak intensity and angle of 2 θ composition variation of 40%,

Angel 2θ (º)	**h k l**	**FWHM**	**Intensity(a.u)**	**Crystal structure**
21,3614	2 0 0	0,307	49.0	*Cubic*
35,8879	3 1 1	0,4093	43.2	*Cubic*
62,9129	4 4 0	0,5117	48.2	*Cubic*

Table 3. The pattern of each peak intensity and angle of 2 θ composition variation of 50%,

Angel 2θ (º)	**h k l**	**FWHM**	**Intensity(a.u)**	**Crystal structure**
30,2391	2 2 0	0,4093	29.1	*Cubic*
35,6496	3 1 1	0,5117	100.0	*Cubic*

43,3047	4 0 0	0,8187	20.4	*Cubic*
57,3706	5 1 1	0,614	27.9	*Cubic*
62,9638	4 4 0	0,5117	36.5	*Cubic*

Table 4. The pattern of each peak intensity and angle of 2 θ composition variation of 60%,

Angel 2θ (^{o})	**h k l**	**FWHM**	**Intensity(a.u)**	**Crystal structure**
30,3073	1 0 4	0,8187	24.0	*Rhombohedral*
35,4873	0 2 1	0,3582	100.0	*Rhombohedral*
43,138	0 2 4	0,8187	28.4	*Rhombohedral*
62,4767	2 0 8	0,4093	25.6	*Rhombohedral*

Table 5. The pattern of each peak intensity and angle of 2 θ composition variation of 70%,

Angel 2θ (^{o})	**h k l**	**FWHM**	**Intensity(a.u)**	**Crystal structure**
35,8695	3 1 1	0,4093	100.0	*Cubic*

Tables 1, 2, 3, and 5 show that the crystal system is Cubic for all variations of 30%, 40%, 50%, 60%, and 70%. Based on the results of the X-ray Diffraction test that has been carried out, it shows the crystal structure, lattice parameters, angle of 2 θ half-peak width (FWHM), etc. The characterization results show that the crystal structure of Fe_3O_4/Polypyrrole nanocomposite is a cubic structure for all variations, but at 60% variation the crystal structure obtained is Rhombohedral and Fe_3O_4/Polypyrrole appears at an angle of 20-30 for all compositions, this is by research [14], which stated that the crystal structure obtained by Fe_3O_4/Polypyrrole is cubic and Fe3O4/Polypyrrole appears at an angle of 20-30. The addition of Polypyrrole into Fe_3O_4 does not affect the resulting crystal structure, this is to research , which states that the addition of polymer to the sample does not affect the crystal structure of Fe_3O_4 nanoparticles.

The XRD test results can also be used to determine the crystal size and microstrain of the nanocomposite. Based on the calculation, the average size of Fe_3O_4/Polypyrrole nanocomposite crystals is obtained as shown in the table,

Table 6. Crystal Size

Fe_3O_4: Polypyrrole Composition	**Crystal SizeD (nm)**
30%	46.73
40%	43.29
50%	31.92
60%	33.23
70%	40.8

From the data obtained by research [15], it is stated that composition variations affect the crystal size of the sample. Based on the analysis of the crystal size obtained, the more Polypyrrole composition, the greater the crystal size, and the more Fe_3O_4 composition added to the Fe_3O_4/Polypyrrole nanocomposite, the greater the crystal size, this statement is by research [9], which states that the more Fe_3O_4 composition which is added to Fe_3O_4/PVDF nanocomposite, the crystal size increases.

The irregular size of the crystals obtained could be due to the uneven homogeneity of the sample by research [15], which said that in addition to the effect of the unequal amount of substance being dripped, the homogeneity

factor and the evenness of the layers also caused the thickness of the layer obtained to be less by the existing theory. Because it also affects the phase that appears.

3.2 MicroStrains

The Fe_3O_4/Polypyrrole micro nanocomposite strain obtained from the calculation results was 0.0098 for the 30% variation, 0.0138 for the 40% variation, 0.0281 for the 50% variation, 0.0278 for the 60% variation, and 0.0055 for the 70% variation. The largest microstrain for all variations of the composition was 0.0281 at 50% composition. The Fe_3O_4/Polypyrrole nanocomposite at 50% variation also has the largest crystal size of 130.4 nm by Table 7 compared to other composition variations. So from the data obtained from the Scherer equation, it states that the crystal size is influenced by the FWHM value, the lower the FWHM value of a diffraction peak produced, the larger the crystal size, this statement is , which states that the lower the FWMH value of an XRD peak, the lower the FWMH value of an XRD peak the larger the crystal size.

Table 7. Comparison of Crystal Size and MicroStrain Values

Fe_3O_4: Polypyrrole Composition	**Crystal Size (nm)**	**MicroStrain (μm)**
30%	46.73	0,0063
40%	43.29	0,0056
50%	31.92	0,0062
60%	33.23	0,0071
70%	40.8	0,0055

Based on the results of calculations on the composition variations of 30%, 40%, 50%, 60%, and 70%, the crystal size and microstrain values were not constant. This is caused by air contamination both in the laboratory and when carrying samples before characterization and during sample making.

IV. CONCLUSION

From the results of research on Microstructure Analysis of Fe_3O_4/Polypyrrole Powder Nanocomposites Synthesized With Sol-Gel Method, it can be concluded that the manufacture of Fe_3O_4/Polypyrrole nanocomposites has been successfully carried out using the sol method with variations in the composition of Fe_3O_4 in Polypyrrole, namely 30%, 40%, 50%, 60%, and 70%, the crystal size is obtained, the more Polypyrrole composition, the greater the crystal size and the smallest crystal size is obtained at 70% variation, due to the slight variation in Fe_3O_4composition, the more Fe_3O_4 composition added to Fe_3O_4/Polypyrrole nanocomposite, the crystal size decreasing. Based on the analysis, it was found that variations in the composition of Fe_3O_4/Polypyrrole affect the value of the microstrain which is found that the larger the crystal size, the easier the dislocation will occur, this causes the hardness value to decrease and the microstrain becomes larger.

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