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Synthesis of PANI/Iron (II, III) Oxide Hybrid Nanocomposites Using SolGel Method

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Abstract: A polyaniline/iron (II,III) (PANI/Fe_3O_4) hybrid nanocomposites were synthesized using a sol-gel method. The characterization of PANI/Fe_3O_4 hybrid nanocomposites were studied by Fourier transforms infrared spectroscopy with attenuated total reflectance (FTIR-ATR), multimeter, and permanent magnet. The FTIR result indicated that the PANI/Fe_3O_4 hybrid nanocomposites were successfully synthesized due to the chemical interaction was occurred by comparing a spectra of Fe_3O_4, polyaniline (PANI) and PANI/Fe_3O_4 hybrid nanocomposites. The electrical conductivity and magnetic properties of PANI/Fe_3O_4 hybrid nanocomposites were clearly performed using a multimeter and a permanent magnet, respectively. Application of external field to the sample have resulted 0.1 mV and 0.001 V DC readings for conductivity. While a Fe_3O_4 in the hybrid nanocomposites shows attractions to the permanent magnet, thus producing a magnetic field.

Keyword: Polyaniline; Fe_3O_4; Sol-gel method.

1. Introduction

Combination of polymer with iron oxide nanoparticles have become tremendously attention in conductive polymer applications due to its structures, chemical and physical properties. It is proved that the hybrid of iron oxide on the network of polymer material provides a better conduction and magnetization due to the production of electromagnetic (EM) field [1]. Polyaniline (PANI) which is derived from a chemical polymerization of analine, is a popular organic conductive polymer used especially for coating applications. By doping of aniline monomer with strong acid has increase the conductivity property of PANI. Emeraldine salt of PANI is identified as conductive compared to the leucomeraldine, emeraldine and pernigraniline which behave as insulator [2]. Due to its advantages, PANI is applied in various applications such as sensor and thermoelectric, drug delivery, waste heat recovery and electronic circuits [3-11]. Many research have been conducting and foreseeing the advantages of inorganic compounds in the PANI matrix especially magnetite (Fe_3O_4) [1217]. Fe_3O_4 shows good ferromagnetism properties and resistance towards the corrosions due to acid solutions [15, 18]. Since Fe_3O_4 is a hydrophobic material, chemical reactions with PANI are increase its dispersions in solution [18]. It is also exhibits good electrical behaviour when external electric field is applied to the material.

In this work, polyaniline/iron (II,III) (PANI/Fe_3O_4) hybrid nanocomposites are synthesized using a sol-gel method. The polymerization of aniline is chemically produced using hydrochloric acid (HCl) as acidic medium and ammonium persulfate ($(NH_4)_2S_2O_8$) as oxidizing agent, thus producing a highly conductive polymer [19]. These PANI/Fe_3O_4 hybrid nanocomposites are prepared using a uniform dispersion of Fe_3O_4 in the nitric acid and deionized water solvent. In order to obtain a nanosize particle, the PANI acts as a coating agent surrounded the surface of the Fe_3O_4 nanoparticles. Based on this work, sol-gel method can produced thin bond-coating excellent adhesion between the Fe_3O_4 and the

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PANI matrix coating as their can glued together in the polymer chains network. To the best of our knowledge, a synthesis of PANI/Fe_3O_4 hybrid nanocomposites based on sol-gel method has never been studied. The synthesis of PANI/Fe_3O_4 hybrid nanocomposites using a sol-gel method is a simple and economic method. A successful characterization of resulting PANI/Fe_3O_4 hybrid nanocomposites is carried out using Fourier transforms infrared spectroscopy with attenuated total reflectance (FTIR-ATR), multimeter, and permanent magnet.

2. Materials and Methods

Materials. In this research, PANI/Fe_3O_4 hybrid nanocomposites were synthesized using a sol-gel method. Fe_3O_4 nanoparticles, nitric acid (HNO_3, Riendemann Schmidt, 65%), ethanol (HmbG Chemicals, 95%), and deionized water were used as a precursor, solvent and catalyst in preparing a Fe_3O_4 sols, respectively. Aniline ($C_6H_5NH_2$, R&M Chemicals), ammonium peroxodisulfate ($(NH_4)_2S_2O_8$, QRëC) and hydrochloric acid (HCl, QRëC, 37%) were used for the production of PANI/Fe_3O_4 hybrid nanocomposites. Tetraethyl orthosilicate (TEOS, Aldrich, 98%) was used for the production of gel in this research. All the chemicals were used as received without further purification.

Synthesis of PANI/Fe_3O_4 Hybrid Nanocomposites. The synthesis procedure of the PANI/Fe_3O_4 hybrid nanocomposites through a sol-gel method as follow: 5 ml Fe_3O_4 sol was sonicated by maintaining the ratio of water to Fe_3O_4 as 4:1. 0.15 g of 0.0016 mol aniline was added dropwise into the sols and resulting aniline/Fe_3O_4 solution after mild stirring using magnetic stirrer. On the other hand, 0.34 g of 0.0015 mol $(NH_4)_2S_2O_8$ was prepared separately into 15 ml of 0.5 M HCl before added into the aniline/Fe_3O_4 solution and producing a dark green PANI/Fe_3O_4 hybrid nanocomposites solution after stirring for 12 hours. Then, a hybrid nanocomposite was centrifuged for 30 times constantly at 4000 rpm for 15 minutes. The precipitation of PANI/Fe_3O_4 hybrid nanocomposites was dried in the oven at 80 °C for 20 hours. A fine powder was obtained by grinding the PANI/Fe_3O_4 hybrid nanocomposites using agate mortar. The gel formation was completed by mixing 5 ml TEOS into 5 ml ethanol, 0.81 ml of 0.1 M HCl and 8 ml deionized water.

Characterization and measurements. Fourier transforms infrared spectroscopy with attenuated total reflectance (FTIR-ATR, PerkinElmer) was used to investigate the functional group region of the PANI/Fe_3O_4 hybrid nanocomposites structure. The electrical conductivity was measured using the 115 Fluke Multimeter at room temperature, and the magnetic properties of the PANI/Fe_3O_4 hybrid nanocomposites was observed using a permanent magnet.

3. Results and Discussions

The identification of chemical interactions, electrical conductivity and magnetic properties on the PANI/Fe_3O_4 hybrid nanocomposites synthesis were successfully investigated. Fig. 1 shows the comparison of FTIR spectra of Fe_3O_4, PANI and PANI/Fe_3O_4 hybrid nanocomposites. The spectrum of PANI shows a peak at 3326 cm^{-1} described the N-H vibrations due to the presence amide. The peak at 1634 cm^{-1} presents in the PANI spectrum indicated that a PANI is obtained at low acidity medium. While a peak at 1052 cm^{-1} shows the presence of sulfonate groups attached to the aromatic rings of PANI. Compared to the PANI/Fe_3O_4 hybrid nanocomposites spectra, it is found a peak at 3228 cm^{-1} (N-H stretching) is slightly disappeared due to a weak vibration, thus a chemical interactions of hybrid nanocomposites attachment are occurred. A peaks at 1567 cm^{-1} and 1488 cm^{-1} represent of C=N and C=C stretching of quinoid and benzeoid rings, respectively. Meanwhile, a peak at 1303 cm^{-1} assigned for C-N secondary aromatic amine stretching. The C-H deformation bond at 1,4-disubstituted benzene ring is confirmed at peaks 1038 cm^{-1}, and 943 cm^{-1}. The differences of peaks shifting on both PANI and PANI/Fe_3O_4 hybrid nanocomposites spectra are occurred due to the weakening in the PANI bonds [15-17,20]. Moreover, the existence of peak at 3338 cm^{-1}, 2919 cm^{-1} and 1463 cm^{-1} , 2850 cm^{-1}, 1709 cm^{-1} and 1089 cm^{-1} are assigned for O-H stretching, C-H stretching, C=C stretching, C=O stretching and C-O stretching bands respective for indicating the acidic medium condition of Fe_3O_4

preparation. A peak at 557 cm^{-1} is represent of a characteristic peak Fe-O stretching band. Most of those peaks are slightly disappeared in the PANI/Fe_3O_4 hybrid nanocomposites spectra, thus showing the hybrid of Fe_3O_4 on the PANI matrixs is successfully formed. A shifted Fe-O stretching band at 512 cm^{-1} in the spectrum of PANI/Fe_3O_4 hybrid nanocomposites also confirming the hybridization interaction.

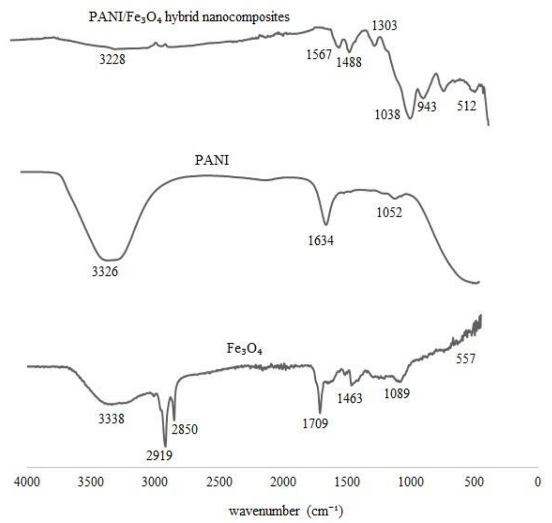

Fig. 1 FTIR spectra of (a) PANI, (b) Fe_3O_4, and (c) PANI/Fe_3O_4 hybrid nanocomposites.

The electrical conductivity of PANI/Fe_3O_4 hybrid nanocomposites was measured using a multimeter. An external electric field was supplied from a simple LED circuit, with 9V battery was applied to the PANI/Fe_3O_4 hybrid nanocomposites. This have increased the movement of the mobile charge in the hybrid nanocomposites and thus increased the conductivity of the PANI/Fe_3O_4 hybrid nanocomposites. The result indicated that the reading values of the conductivity of the PANI/Fe_3O_4 hybrid nanocomposites are 0.001 volt (V) and 0.1 millivolt (mV). These difference reading values occurred due to the decreasing of the mobile charge movement in the hybrid after the external electric field was closed. The magnetic interaction between the permanent magnet and the PANI/Fe_3O_4 hybrid nanocomposites have formed a magnetic field as shown in Fig. 2. Ferromagnetism in the PANI/Fe_3O_4 hybrid nanocomposites is existed due to the presence of the Fe_3O_4 proved that the magnetic properties of the PANI/Fe_3O_4 hybrid nanocomposites as the alignment of the charge electrons around the permanent magnet. This alignment of charge electrons has created a magnetic field in the PANI/Fe_3O_4 hybrid nanocomposites.

Fig. 2 Formation of magnetic field due to interactions of permanent magnet and PANI/Fe_3O_4 hybrid nanocomposites powder.

4. Conclusion

PANI/Fe_3O_4 hybrid nanocomposites were synthesized using a sol-gel synthesis method through the hybrid of well dispersed Fe_3O_4 nanoparticles onto the polymerized aniline. The synthesis of PANI/Fe_3O_4 hybrid nanocomposites were confirmed successful based on characterization of FTIR-ATR result. Through a sol-gel method, a PANI/Fe_3O_4 hybrid nanocomposites were found electrically conductive and magnetically properties. Therefore, it is possible to prepare a hybrid nanocomposites using a sol-gel method and possibly attractive its applications in the sensors and drug delivery technology.

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