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

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Abstract: A polyaniline/iron (II,III) (PANI/Fe₃O₄) hybrid nanocomposites were synthesized using a sol-gel method. The characterization of PANI/Fe₃O₄ 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/Fe₃O₄ hybrid nanocomposites were successfully synthesized due to the chemical interaction was occurred by comparing a spectra of Fe₃O₄, polyaniline (PANI) and PANI/Fe₃O₄ hybrid nanocomposites. The electrical conductivity and magnetic properties of PANI/Fe₃O₄ 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 Fe₃O₄ in the hybrid nanocomposites shows attractions to the permanent magnet, thus producing a magnetic field.

Keyword: Polyaniline; Fe₃O₄; 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 aniline, 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 (Fe₃O₄) [1217]. Fe₃O₄ shows good ferromagnetism properties and resistance towards the corrosions due to acid solutions [15, 18]. Since Fe₃O₄ 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/Fe₃O₄) 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 ((NH₄)₂S₂O₈) as oxidizing agent, thus producing a highly conductive polymer [19]. These PANI/Fe₃O₄ hybrid nanocomposites are prepared using a uniform dispersion of Fe₃O₄ 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 Fe₃O₄ nanoparticles. Based on this work, sol-gel method can produced thin bond-coating excellent adhesion between the Fe₃O₄ and the
PANI matrix coating as their can glued together in the polymer chains network. To the best of our knowledge, a synthesis of PANI/Fe$_3$O$_4$ hybrid nanocomposites based on sol-gel method has never been studied. The synthesis of PANI/Fe$_3$O$_4$ hybrid nanocomposites using a sol-gel method is a simple and economic method. A successful characterization of resulting PANI/Fe$_3$O$_4$ 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$_3$O$_4$ hybrid nanocomposites were synthesized using a sol-gel method. Fe$_3$O$_4$ nanoparticles, nitric acid (HNO$_3$, Riedemann Schmidt, 65%), ethanol (HmbG Chemicals, 95%), and deionized water were used as a precursor, solvent and catalyst in preparing a Fe$_3$O$_4$ sols, respectively. Aniline (C$_6$H$_5$NH$_2$, R&M Chemicals), ammonium peroxodisulfate ((NH$_4$)$_2$S$_2$O$_8$, QRëC) and hydrochloric acid (HCl, QRëC, 37%) were used for the production of PANI/Fe$_3$O$_4$ 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$_3$O$_4$ Hybrid Nanocomposites. The synthesis procedure of the PANI/Fe$_3$O$_4$ hybrid nanocomposites through a sol-gel method as follow: 5 ml Fe$_3$O$_4$ sol was sonicated by maintaining the ratio of water to Fe$_3$O$_4$ as 4:1. 0.15 g of 0.0016 mol aniline was added dropwise into the sols and resulting aniline/Fe$_3$O$_4$ solution after mild stirring using magnetic stirrer. On the other hand, 0.34 g of 0.0015 mol (NH$_4$)$_2$S$_2$O$_8$ was prepared separately into 15 ml of 0.5 M HCl before added into the aniline/Fe$_3$O$_4$ solution and producing a dark green PANI/Fe$_3$O$_4$ 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$_3$O$_4$ hybrid nanocomposites was dried in the oven at 80 °C for 20 hours. A fine powder was obtained by grinding the PANI/Fe$_3$O$_4$ 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$_3$O$_4$ hybrid nanocomposites structure. The electrical conductivity was measured using the 115 Fluke Multimeter at room temperature, and the magnetic properties of the PANI/Fe$_3$O$_4$ 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$_3$O$_4$ hybrid nanocomposites synthesis were successfully investigated. Fig. 1 shows the comparison of FTIR spectra of Fe$_3$O$_4$, PANI and PANI/Fe$_3$O$_4$ 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$_3$O$_4$ 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$_3$O$_4$ 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$_3$O$_4$.
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\(_3\)O\(_4\) hybrid nanocomposites spectra, thus showing the hybrid of Fe\(_3\)O\(_4\) on the PANI matrix is successfully formed. A shifted Fe-O stretching band at 512 cm\(^{-1}\) in the spectrum of PANI/Fe\(_3\)O\(_4\) hybrid nanocomposites also confirming the hybridization interaction.

The electrical conductivity of PANI/Fe\(_3\)O\(_4\) 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\(_3\)O\(_4\) hybrid nanocomposites. This have increased the movement of the mobile charge in the hybrid nanocomposites and thus increased the conductivity of the PANI/Fe\(_3\)O\(_4\) hybrid nanocomposites. The result indicated that the reading values of the conductivity of the PANI/Fe\(_3\)O\(_4\) 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\(_3\)O\(_4\) hybrid nanocomposites have formed a magnetic field as shown in Fig. 2. Ferromagnetism in the PANI/Fe\(_3\)O\(_4\) hybrid nanocomposites is existed due to the presence of the Fe\(_3\)O\(_4\) proved that the magnetic properties of the PANI/Fe\(_3\)O\(_4\) hybrid

Fig. 1 FTIR spectra of (a) PANI, (b) Fe\(_3\)O\(_4\), and (c) PANI/Fe\(_3\)O\(_4\) hybrid nanocomposites.

4. Conclusion
PANI/Fe\(_3\)O\(_4\) hybrid nanocomposites were synthesized using a sol-gel synthesis method through the hybrid of well dispersed Fe\(_3\)O\(_4\) nanoparticles onto the polymerized aniline. The synthesis of PANI/Fe\(_3\)O\(_4\) hybrid nanocomposites were confirmed successful based on characterization of FTIR-ATR result. Through a sol-gel method, a PANI/Fe\(_3\)O\(_4\) 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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References

[1] Wan, M. X. & Li, J. C. (1999) Electrical and Ferromagnetic Behaviour of Polyaniline Composites, Synthetic Metals, Vol. 101, pp. 844845.

[2] Negi, Y. S. & Adhyapak, P. V. (2002) Development In Polyaniline Conducting Polymers, Journal of Macromolecular Science – Polymer Reviews, Vol. 42(1), pp. 35-53.

[3] Debarnot, D. N. & Porcin-Epaillard, F. (2003) Polyaniline as a New Sensitive Layer For Gas Sensor, Analytica Chimica Acta, Vol. 475, pp. 1-15.

[4] Sengupta, P. P., Barik, S. & Adhikari, B. (2006) Polyaniline as A Gas-Sensor Material, Materials and Manufacturing Processes, Vol. 21, pp. 263-270.

[5] Huang, Z. M., Zhang, Y. Z., Kotaki, M. & Ramakrishna, S. (2003) A Review on Polymer Nanofibers by Electrospinning and Their Applications in Nanocomposites, Composites Science and Technology, Vol. 63, pp. 2223-2253.

[6] Llorens, E., Armelin, E., Mar PérezMadrigal, M., Valle, L. J., Alemán, C. & Puiggalí, J. (2013) Nanomembranes and Nanofibers From Biodegradable Conducting Polymers, Polymers, Vol. 5, pp. 1115-1157.

[7] Park, C. S., Lee, C. & Kwon, O. S. (2016) Conducting Polymer Based Nanobiosensors, Polymers, Vol. 8 (249), pp. 1-18.

[8] Culebras, M., Gomez, C. M. & Cantarero, A. (2014) Review on Polymers for Thermoelectric Applications, Materials, Vol. 7 (9), pp. 6701.

[9] Roussel, F., King, R. C. Y., Kurikose, M., Depriester, M., Hadj-Sahraoui, A., Gors, C., Addad, A. & Brun, J. (2014), Electrical and Thermal Transport Properties of Polyaniline/Silver Composites and Their Use as Thermoelectric Materials, Synthetic Metals, Vol. 199, pp. 196-204.

[10] Kolasinska, E. & Kolasinski, P. (2016) A Review on Electroactive Polymers for Waste Heat Recovery, Materials, Vol. 9 (485), pp. 1-15.

[11] Huang J. (2006) Synthesis and Applications of Conducting Polymer Polyaniline Nanofibers, Pure Applied Chemical, 78 (1), pp. 15-27.

[12] Xuan, S., Wang, Y. X. J., Yu, J. C. & Leung, K. C. F. (2009) Preparation, Characterization, and Catalytic Activity of Core/Shell Fe3O4@ Polyaniline@ Au Nanocomposites, Langmuir, Vol. 25(19), pp. 118311843.

[13] Araujo, A. C. V., Oliveira, R. J., Junior, S. A., Rodrigues, A. R., Machado, F. L. A., Cabral, F. A. O. & Azevedo, W. M. (2010) Synthesis Characterization and Magnetic Properties of PolyanilineMagnetite Nanocomposites, Synthetic Metals, Vol. 160, pp. 685-690.

[14] Zhang, Y. J., Lin, Y. W., Chang, C. C. & Wu, T. M. (2010) Magnetic Properties of Hydrophilic Iron Oxide/Polyaniline Nanocomposites Synthesized by In Situ Chemical Oxidative Polymerization, Synthetic Metals, Vol. 160, pp. 1086-1091.

[15] Sim, B., Chae, J. S. & Choi, H. J. (2015) Fabrication of Polyaniline Coated Iron Oxide Hybrid Particles and Their Dual Stimuli-Response Under Electric and Magnetic Fields, Express Polymer Letters, Vol. 9(8), pp. 736743.

[16] Adamu, M. A., Mustafa, M. K. & Ruslan, N. N. (2016) Morphology of Polyaniline Nanotube with Various Level of Fe3O4 Nanoparticles and Their Electrical Conductivities by Ultrasonic Dispersion Method, ARPN Journal of Engineering and Applied Sciences, Vol. 11(16), pp. 9725-9729.

[17] Khan, A., Aldawayyan, A. S., Alhoshan, M. & Alsalhi, M. (2010) Synthesis by In Situ Chemical Oxidatice Polymerization and Characterization of Polyaniline/Iron Oxide Nanoparticle Composite, Polymer International, Vol. 59, pp. 1690-1694.

[18] Tudorache, F. & Grigoras, M. (2010) Study of Polyaniline-Iron Oxides Composites Using For Gas Detection, Optoelectronics and
Advanced Materials-Rapid Communications, Vol. 4(1), pp. 43-47.

[19] Katoch, A., Burkhart, M., Hwang, T. & Kim, S. S. (2012) Synthesis of Polyaniline/TiO₂ Hybrid Nanoplates via A Sol-Gel Chemical Method, Chemical Engineering Journal, Vol. 192, pp. 262-268.

[20] Liu, R., Qiu, H., Zong, H. & Fang, C. (2012) Research Article: Fabrication and Characterization of Composite Containing HCl-Doped Polyaniline and Fe Nanoparticles, Journal of Nanomaterials, Vol. 2012, pp. 1-7.