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Interfacial Polymerization and Characterization of Poly (2-Chloroaniline)-Nife$_2$o$_4$ Nanocomposite

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Abstract
Due to an increase in the demand of power technologies for portable electronics, conductive polymers integrated with inorganic metal oxides have emerged as materials for energy storage and conversion devices such as batteries and fuel cells. In this study, binary metal oxide was prepared by simple co precipitation method and mixed with poly(2-chloroaniline) *via* interfacial polymerization. The resulting nanocomposite material was characterized by X-ray diffraction (XRD), Fourier Transform Infrared spectroscopy (FT-IR) and Ultraviolet - Visible spectroscopy (UV-Vis) and EDAX. The thermal stability of the nanocomposite was investigated by thermogravimetric analysis (TGA).

Keywords
nanocomposite, interfacial polymerization, metal oxide, poly(2-chloroaniline)

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INTRODUCTION:
Rapid increase in global energy use and growing environmental concerns have prompted in the development of low-cost, efficient, safer, environmentally benign materials for electrochemical energy conversion and storage. Some electrochemical devices like fuel cells, batteries, and super capacitors show great promise for large scale energy conversion and storage applications.

Conducting polymers are competing materials for organic-inorganic hybrid composites in lithium batteries due to their electrical conductivity and high coulombic efficiency. Among the conducting polymers, poly(3,4-ethylenedioxythiophene), polypyrrole and polyaniline, have attracted great interest in energy storage, sensors and electrochromic devices since the discovery in 1960. [1]

Many transition metal oxides such as $LiCoO_2$ and $LiNiO_2$ have been investigated as cathode materials for lithium ion batteries. [2] Metal oxides usually have the lithium storage properties but lacking in the conductivity and cyclability that are vital for industrial applications.

Metal oxide modified conducting polymers which result due to the incorporation of conducting polymer with inorganic redox oxide act as a hybrid or composite, suitable for electrochemical Li intercalation and is used as electrodes for rechargeable lithium batteries. The successful incorporation of inorganic moieties into the conducting polymer matrix enhances the electron transfer rate at the modified surface/electrolyte interface. [3]

Young-Min et al prepared polyaniline/ $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (LNCA) composite by *in situ* self-stabilized dispersion polymerization in the presence of LNCA and showed good reversibility for Li insertion in discharge cycles when used as the electrode of lithium ion batteries. [4]

In this paper we attempt to synthesize a new nanocomposite material using poly(2-chloroaniline) and nickel ferrite by interfacial polymerization. The nanocomposite was characterized by different techniques and suggested as a promising electrode material in Li ion batteries.

MATERIALS AND METHODS

All the chemicals were of analytical grade purchased and used without any further purification. The synthesized poly(2-chloroaniline)-$NiFe_2O_4$ nanocomposite was characterized by field-emission scanning electron microscopy (FESEM) equipped with an energy dispersive spectroscope, X-ray diffraction (XRD), Fourier transform infrared spectrometry (FTIR), UV-spectra and thermogravimetric analysis.

Synthesis of nickel ferrite

The nickel ferrite is prepared by simple coprecipitation method. [5, 6] The precursor of Ni and Fe salts ($NiCl_2.6H_2O$ and $FeCl_3{\cdot}6H_2O$) were dissolved in deionized water under vigorous stirring. The resulting solution was mixed with an aqueous solution of ammonia (0.6 M) under vigorous stirring for 20 min at a pH of 11-12. [7] The resulting precipitate was centrifuged and then filtered, washed with warm distilled water several times for removing excess ions. The precipitate was then dried in air at 110◦C and subjected to different calcination temperatures of 300, 400, 500 and 600°C in air atmosphere for 6 hours with a ramp rate of 3°C/min.

Preparation of poly(2-chloroaniline) and its metal oxide nanocomposite

The typical procedure for the synthesis of poly(2-chloroaniline) *via* interfacial polymerization was carried out as follows: 2-chloroaniline was dissolved in 100 ml CCl_4 and the oxidant ammonium persulfate was dissolved in 100 ml of 1 M HCl solution. Each solution was magnetically stirred for an hour. Then the oxidant solution was then carefully transferred to the monomer (2-chloroaniline) solution. After a short induction time, the reaction took place and the poly(2-chloroaniline) was initially formed at the interface of the immiscible solutions. After 24 hours at room temperature, the resulting precipitate was filtered, rinsed with deionized water several times, and the product was dried for 24 hours. For the preparation of the poly(2-chloroaniline)-$NiFe_2O_4$ composite, the metal oxide was mixed with 2-chloroaniline solution initially and the same procedure was followed.

RESULTS:

UV-Visible spectra

The UV-Visible spectra of poly(2-chloroaniline) and poly(2-chloroaniline)-$NiFe_2O_4$ (Fig 1), exhibit the π-π* transition of the benzenoid rings at 336 nm and at 630 nm shows the n-π* transition of quinonoid rings similar to the report of Yavuz. [8] The quinonoid band plays a key role in switching poly(2-chloroaniline) from an electric insulator to a conductor upon doping.

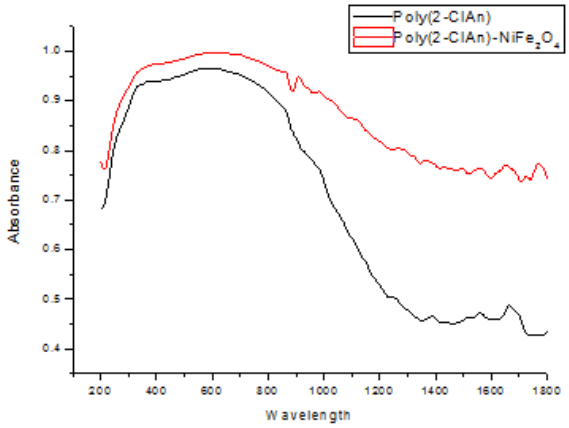

Figure 1: UV- Visible spectra of poly(2-chloroaniline) and poly(2-chloroaniline)-$NiFe_2O_4$

FTIR spectra

The FTIR spectrum of poly(2-chloroaniline) show bands at 3226, 1286, 1564, 1492, 744 cm^{-1} (Fig 2) corresponding to poly(2-chloroaniline). The bands corresponding to N-H stretching vibration appear at 3226 cm^{-1}. The bands corresponding to stretching

vibrations of N-B-N and N=Q=N structure appear at 1492 and 1564 cm^{-1}, respectively (-B- and =Q= stands for benzenoid and quinoid moieties respectively), C-Cl stretching vibration is observed at 744 cm^{-1}. [9]

In the poly(2-chloroaniline)-$NiFe_2O_4$ nanocomposite, bands due to N-H, C-N, C=C (quininoid) stretching vibrations are shifted towards higher wavenumber. Bands due to C=C stretching of benzenoid and C-Cl stretching are shifted towards lower wavenumber.

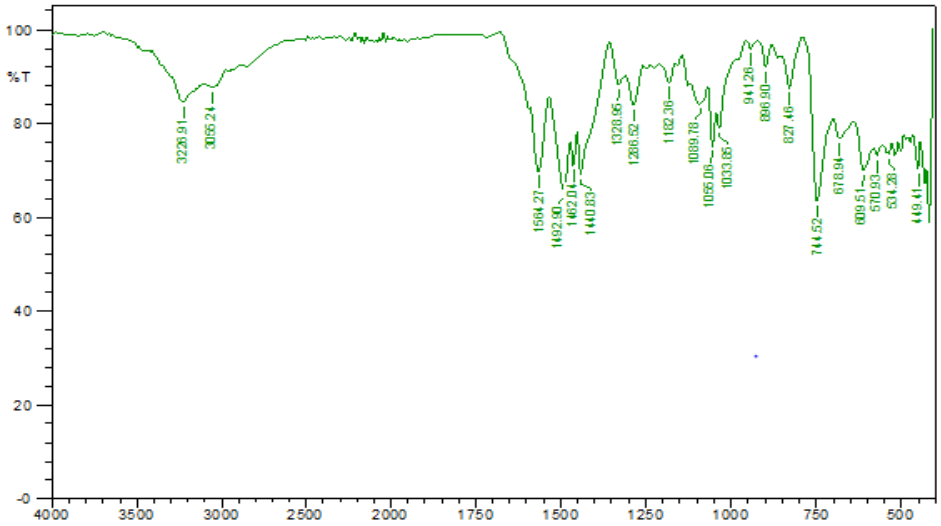

Figure 2: FTIR spectrum of poly(2-chloroaniline)

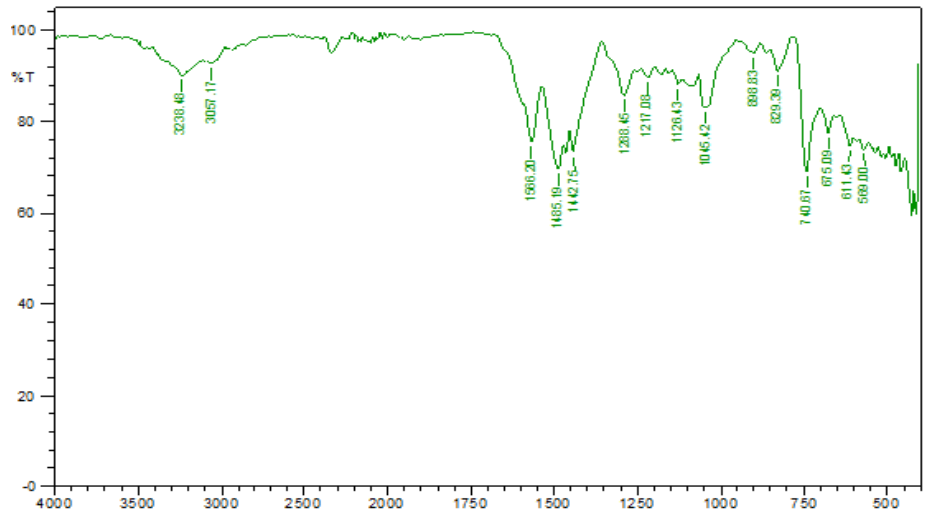

Figure 3:FTIR spectrum of poly(2-chloroaniline)-$NiFe_2O_4$ composite

XRD analysis

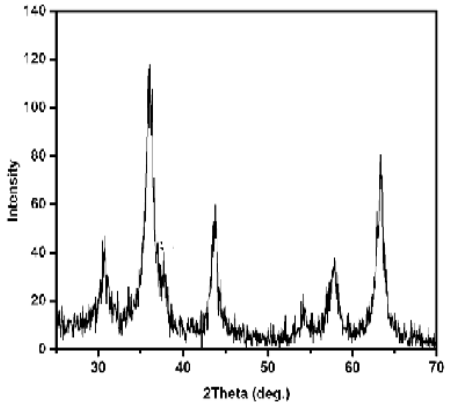

Figure 4

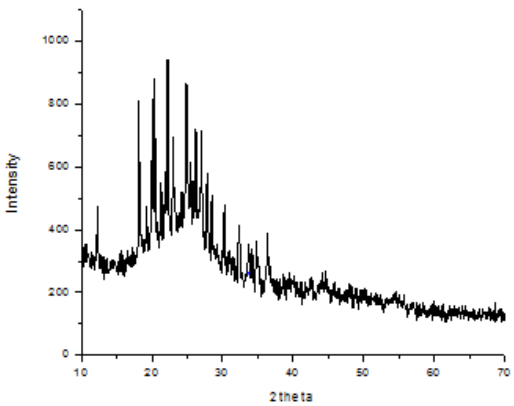

Figure 5

X-ray diffraction pattern of pure $NiFe_2O_4$ & poly (2-chloroaniline)-$NiFe_2O_4$ composite

Figure 4 shows the XRD pattern of $NiFe_2O_4$ cubic spinel (JCPDS Card No. 10-0325). [10]

TGA analysis

In the TGA of poly(2-chloroaniline)-$NiFe_2O_4$ composite (Fig 5), there is a three-step weight loss. The first degradation is due to moisture evaporation, which is bound to the surface of the polymer, second degradation is due to the release of dopants and last stage is due to the complete decomposition of the organic part of the composites. The decomposition temperature of poly (2-chloroaniline)-$NiFe_2O_4$ composite is then compared with PANI- $NiFe_2O_4$. This shows that the interaction of $NiFe_2O_4$ with poly(2-chloroaniline) matrix increases its thermal stability which agrees well with the results obtained by Wang et al. [11]

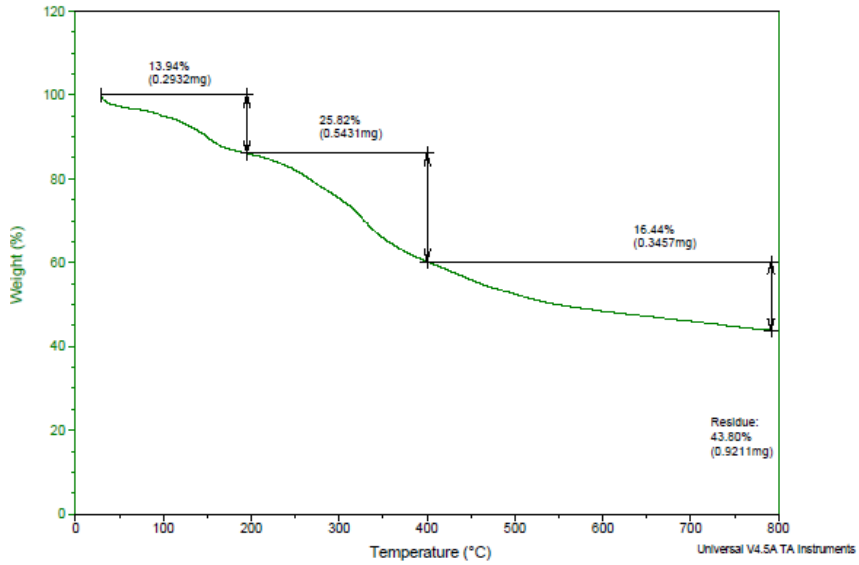

Figure 5: TGA of poly(2-chloroaniline)-$NiFe_2O_4$

FE-SEM Analysis

FESEM was performed to investigate the surface morphology of the polymer nanocomposite. EDAX was done to reveal the chemical composition of the nanocomposite. The SEM image of poly(2-chloroaniline)-$NiFe_2O_4$ nanocomposite appears rod like structure and completely different from pure nickel ferrite of uniform sphere-like shaped reported by Prasanna et al. [12]

Thus poly(2-chloroaniline) layers are completely embedded on the surface of $NiFe_2O_4$ nanoparticles appearing as small aggregated globules. [13, 14]

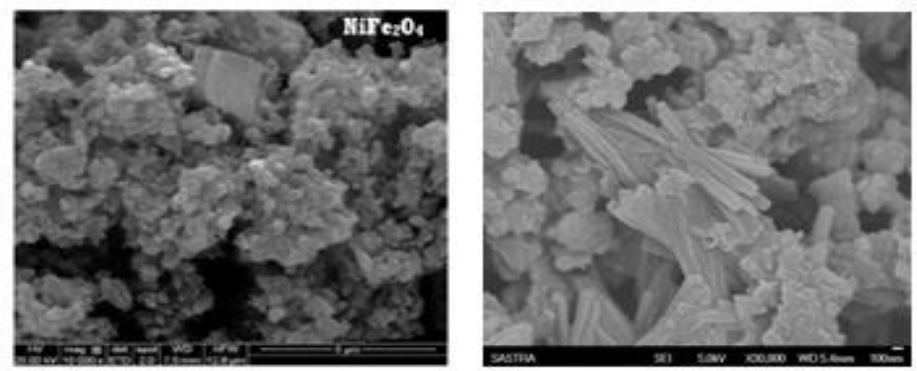

Figure 6 and Figure 7

SEM image of pure $NiFe_2O_4$ and poly(2-chloroaniline)-$NiFe_2O_4$

The EDX result shows that $NiFe_2O_4$ was present in the nanocomposite and the weight percentages are shown in the table 1.

Table 1: Elemental composition of poly(2-chloroaniline)-$NiFe_2O_4$

Element	Weight %	Atomic %
C K	30.51	71.55
O K	13.72	24.16
Cl K	4.96	3.94
Fe K	0.53	0.26
Ni K	0.17	0.08

DISCUSSION:

From the UV-Visible spectrum, the absorption peak which is observed at 850 nm is due to polaron/bipolaron transition indicating the interaction of polymer chains and metal oxide particles. Some of the peaks observed in poly(2-chloroaniline) nickel ferrite nanocomposite in the IR spectrum show shifts towards higher and lower wavenumbers. The peaks observed between 400 and 700 cm^{-1} correspond to Fe–O bonding of metal oxide. This confirms the interaction of metal oxide in the polymeric matrix. [15] The thermogravimetric analysis reveals that the thermal stability of the composite is higher than that of poly(2-chloroaniline) and shows the interaction between $NiFe_2O_4$ particles and polyaniline chains. [16] The XRD of the composite shows a decrease in crystallinity due to the incorporation of poly(2-chloroaniline) chains into the agglomerates of $NiFe_2O_4$ particles.The SEM results show that the synthesized material has particle size of nanometer scale. The elemental composition confirms the trace amounts of iron and nickel present in it.

CONCLUSION

Poly(2-chloroaniline)-$NiFe_2O_4$ nanocomposite was synthesized *via* interfacial polymerization and characterized by UV-Visible spectroscopy, FTIR spectroscopy, XRD, TGA and FESEM. The UV and FTIR spectral data confirm that there is an strong interaction between metal oxide $NiFe_2O_4$ and poly(2-chloroaniline) chains. The thermal stability was studied by thermogravimetric analysis and the SEM image shows greater agglomeration and the average particle size of nanocomposite is found to be 100 nm. The elemental composition was recorded by energy dispersive X-ray analysis and confirms the presence of iron and nickel in the nanocomposite.

REFERENCES

[1] Bhadra S, Khastgir D, Singha N K, Lee J H., Progress in preparation, processing and applications of polyaniline, Progress in Polymer Science, 34:783-810 (2009)

[2] Michalska M, Lipinska L, Mirkowska M, Aksienionek M, Diduszko R, Wasiucionek M., Nanocrystalline lithium–manganese oxide spinels for Li-ion batteries-Sol-gel synthesis and characterization of their structure and selected physical properties, Solid State Ionics 188: 160-164 (2011)

[3] Ballarin B, Masiero S, Seeber R, Tonelli D, Journal of Electroanalytical Chemistry, 449 (1–2): 173 (1998)

[4] Young-Min Chung and Kwang-Sun Ryu, Electrochemical Properties of $LiNi0.8Co0.15Al0.05O_2$ coated with polyaniline, Bulletin of the Korean Chemical Society, Vol. 30, No. 8 1733 (2009)

[5] Goldman A, Laing A M., Journal of Physical and Colloid chemistry, 4 C1 297**(**1977)

[6] Attaie A, Piramoon M R, Harris I R, Ponton C B., Journal of Material Science, 30: 5600 (1995)

[7] Sophie L, Delphine F, Marc P, Alain R, Caroline R, Luce V E, Robert N M., Magnetic iron oxide nanoparticles: synthesis, stabilization, vectorization, physicochemical characterization, and biological applications, Chemical Reviews, vol. 108, 2064-2110 (2008)

[8] Yavuz A G, Gok A., Preparation of TiO_2/PANI composites in the presence of surfactants and investigation of electrical properties, Synthetic Metals, 157:235–242 (2007)

[9] Porselvi Linganathan, Jhancy Mary Samuel, Effect of dodecyl benzene sulphonic acid on the electrical conductivity behaviour of poly(2-chloroaniline) and poly(2-chloroaniline)/Silk blends, American Journal of Polymer Science, 4(4): 107-116 (2014)

[10] Costa ACFM, Leite AMD, Ferreira HS, Kiminami RHGA, Cavac S, Gama L. Brown pigment of the nanopowder spinel ferrite prepared by combustion reaction, Journal of European Ceramic Society, 28: 2033-2037 (2008)

[11] Wang S, Tan Z, Li Y, Sun L, Zhang T., Synthesis, characterization and thermal analysis of polyaniline/ZrO_2 composites, Thermochimica Acta, 441: 191-194 (2006)

[12] Prasanna G D, Ashok R L, Prasad V B and Jayanna H S, Synthesis and characterization of magnetic and conductive nickel ferrite–polyaniline nanocomposites, Journal of Composite Materials, (2014)

[13] Prasanna G D, Jayanna H S, Lamani A R, Polyaniline/$CoFe_2O_4$ nanocomposites: A novel synthesis, characterization and magnetic properties, Synthetic Metals, 161: 2306–2311 (2011)

[14] Jing Jiang., Facile Synthesis and Characterization of Polyaniline/$NiFe_2O_4$ Nanocomposite in w/o Microemulsion, Journal of Macromolecular Science, Part B: Physics, 47: 242–249 (2008)

[15] Raksha Sharma, Rakesh Malik, Subhalakshmi Lamba and Annapoorni S, Metal oxide/polyaniline nanocomposites: Cluster size and composition dependent structural and magnetic properties, Bulletin of Materials Science, Vol. 31, No. 3, 409–413 (2008)

[16]. S. Wang, Z. Tan, Y. Li, L. Sun and T. Zhang, Synthesis, characterization and thermal analysis of polyaniline/ZrO_2 composites, Thermochimica Acta, 441, (2006), pp. 191-194.