

# Electrochemical Performance of Surfactant Assisted Hematite Nanoparticles by Chemical Synthesis Method

S. Ezhil Arasi, P. Devendran, A. Arivarasan

**Abstract:** *Fe<sub>2</sub>O<sub>3</sub> nanoparticles were prepared by simple chemical route. The structural, functional, morphological properties of prepared nanoparticles were obtained by Powder X-ray Diffraction analysis, Fourier transform infrared spectroscopy, and Scanning Electron Microscopy analysis respectively. The average grain size of the prepared nanoparticles was calculated using the Scherrer formula. The functional groups and metal bonding were analyzed through FTIR analysis. The external morphology of the prepared nanomaterials was analyzed with scanning electron microscopy technique. Electrochemical property of the prepared nanomaterial was examined with the help of cyclic voltammetry, galvanostatic charge-discharge and electrochemical impedance spectroscopy.*

**Keywords:** Hematite Nanoparticles, XRD, Electrochemical studies, Pseudocapacitor.

## I. INTRODUCTION

A present promising candidate, alternative source of energy is the energy storage device like supercapacitors. The application of supercapacitors has been emerged by their low energy density [1]. There have been larger efforts spend on increasing the energy density by the researchers. And hence the research interest has been increased in maximizing the development of positive and negative electrode with higher specific capacitance [2], [3]. In past few decades, the role of transition metal oxides has been enormously increasing for their excellent optical and electrical properties which made it for utilizing in various applications such as energy storage devices, catalysis, photo-degradation etc., [4], [5]. The nano-particles with magnetic properties have attracted many researchers for their typical physical and chemical properties. By modifying the structure of nanoparticles, the properties and applications can be varied. Among various magnetic materials, hematite (Fe<sub>2</sub>O<sub>3</sub>) nanoparticles has been widely synthesized and used in many applications [5], [6]. Also, it is an eco-friendly material that

Revised Manuscript Received on December 29, 2019.

\* Correspondence Author

**S. Ezhil Arasi**, Department of Physics, Kalasalingam Academy of Research and Higher Education, Krishnankoil, Tamil Nadu 626126, India. Email: arasi1105@gmail.com

**P. Devendran**, Department of Physics, Kalasalingam Academy of Research and Higher Education, Krishnankoil, Tamil Nadu 626126, India. Email: pdevavenmani@gmail.com

**A. Arivarasan\***, Department of Physics, Kalasalingam Academy of Research and Higher Education, Krishnankoil, Tamil Nadu 626126, India. Email: arivarasan.nanotech@gmail.com

is more stable and neutral in all alkaline solutions. Since the iron oxide nanomaterials possess excellent theoretical capacitance values, it can be used as an modified electrode material for a supercapacitor. In general, the hematite nanoparticles can be pre-pared by various techniques such as combustion method, sol-gel technique [7], hydrothermal [8], etc., Of all these methods, simple chemical technique is the most common among many researchers as it is done in ordinary room temperature with mild conditions. Iron oxides exhibits variety of nanostructures [9]. Though various structures were available, the quasi spheres like structure exhibits better electrochemical behaviour. The iron oxide nanoparticles show excellent theoretical capacitance of about 382.7 mF/cm<sup>2</sup> at 0.5 mA/cm<sup>2</sup> [10], [11]. In this study, the magnetic Fe<sub>2</sub>O<sub>3</sub> nanoparticles were prepared through a cost-effective chemical method and characterized by PXRD, FTIR and SEM analysis from which the crystal structure, functional group analysis and surface morphology were examined. Electrochemical applications of the prepared surfactant assisted hematite nanoparticles were observed using the cyclic voltammetry, galvanostatic charge discharge, electro-chemical impedance spectroscopic studies [12].

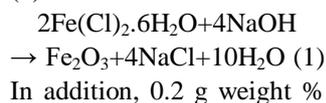
## II. EXPERIMENTAL SECTION

### A. Chemicals

Analytical grade Iron (III) chloride hexa hydrate Fe(Cl)<sub>2</sub>.6H<sub>2</sub>O, was used as the precursors, polyvinylpyrrolidone (PVP), sodium hydroxide (NaOH) and ethanol were purchased from Sisco Research Laboratories Pvt. Ltd., Mumbai, India. All the chemicals with analytical grade was used as purchased. The entire reaction and electrolyte solutions were freshly prepared with deionized (DI) water. All the synthesis procedures were carried out in room temperature.

### B. Preparation of hematite nanoparticles

Facile Fe<sub>2</sub>O<sub>3</sub> nanoparticles was prepared using Iron (III) chloride hexa hydrate Fe(Cl)<sub>2</sub>.6H<sub>2</sub>O as precursor material. Stoichiometric amount of Fe(Cl)<sub>2</sub>.6H<sub>2</sub>O was dissolved in 100 ml DI water. Aqueous solution of NaOH was added drop-wise in order to maintain the pH of reaction mixture at 7. The reaction mechanism was given in equation (1).



of PVP was added in the resultant solution as surfactant and allowed to constant stir up to 1h.

The precipitate obtained was centrifuged many times with DI water and ethanol to remove the unwanted materials or additives present in the sample. Thus, the acquired precipitate was further air dried at ambient temperature then, calcinated at 300°C for 3 h to improve the crystallinity of sample.

### C. Characterizations and modified electrode fabrication

The prepared hematite nanoparticles were characterized by powder X-ray diffraction analysis, Crystalline nature of prepared Fe<sub>2</sub>O<sub>3</sub> nanoparticles were confirmed by powder X-ray diffraction analysis (PXRD) using Bruker X-ray diffractometer (D8 advance ECO) with monochromatic Cu-K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). Surface morphology of Fe<sub>2</sub>O<sub>3</sub> nanoparticles was analyzed using ZEISS-EVO 18 Research, Japan, and Scanning Electron Microscope (SEM). sample Fourier transform infrared spectrometer (FTIR) was employed using a Shimadzu (IR Tracer-100) spectrophotometer within the range of 4000– 400 cm<sup>-1</sup> using KBr pellet system. Electrochemical analysis such as cyclic voltammetry, galvanostatic charge-discharge and electrochemical impedance spectroscopy were examined with the help of electrochemical workstation (CH instrument, CHI 6008e, USA). The workstation was three electrode system provided with Ag/AgCl reference electrode, platinum wire as counter electrode and a modified electrode made of prepared nanomaterials. The electrolyte solution was made of aqueous solution of 1 M KOH. The doctor blade technique was used to fabricate the modified electrode material.

## III. RESULTS AND DISCUSSION

### A. X-Ray Diffraction analysis

The crystalline structure of prepared PVP assisted Fe<sub>2</sub>O<sub>3</sub> nanoparticles was examined by powder X-ray diffraction analysis. The PXRD pattern of prepared PVP assisted Fe<sub>2</sub>O<sub>3</sub> nanoparticles were shown in Fig.1. The range was fixed between 10-80°. The peaks were in good accordance with the bulk Fe<sub>2</sub>O<sub>3</sub> (JCPDS card number #89-8104) [13]. Eight different maximum peaks were observed in prepared PVP assisted Fe<sub>2</sub>O<sub>3</sub> nanoparticles. The  $2\theta$  values and their corresponding hkl indices were 24.213° (012), 33.255° (104), 35.722° (110), 40.973° (113), 49.602° (024), 54.232° (116), 62.615° (214), 64.178° (300) respectively. Broader peak suggests that the prepared sample were in nano size with rhombohedral crystal structure. The space group of prepared PVP assisted Fe<sub>2</sub>O<sub>3</sub> nanoparticles was found to be R3c(167) with cell parameters  $a=5.023 \text{ \AA}$ ,  $c=13.708 \text{ \AA}$ . The grain size of prepared PVP assisted Fe<sub>2</sub>O<sub>3</sub> nanoparticles were ~12 nm.

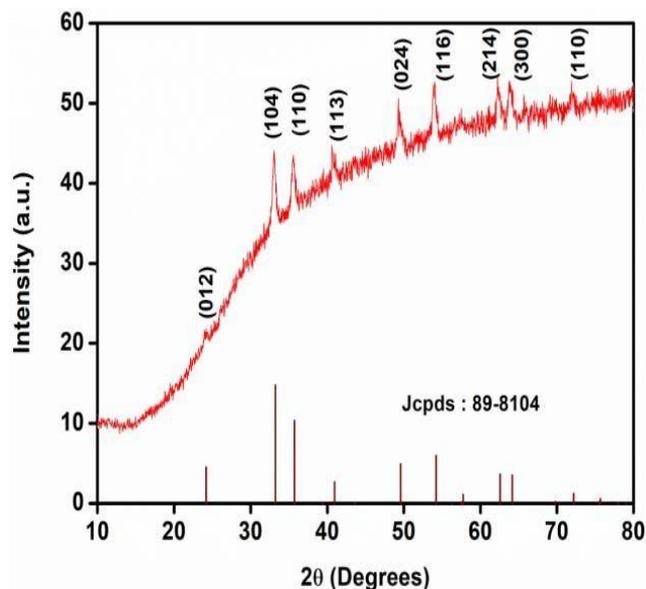


Fig. 1. XRD patterns of PVP assisted Fe<sub>2</sub>O<sub>3</sub> nanoparticles

### B. Fourier Transform Infra-Red spectral analysis

The functional groups and metal bonding were identified through the FTIR spectrum. Fig. 2. Shows the FTIR spectrum of the prepared hematite nanoparticles. Region between 800 to 400 was due to metal oxygen M-O lattice bonding vibrations. The vibrational modes of Fe-O were confirmed through the emergence of peaks at 480 cm<sup>-1</sup>, 540 cm<sup>-1</sup>. The peak at 590 and 786 cm<sup>-1</sup> was due to the Fe-O-Fe bonding vibrations [14].

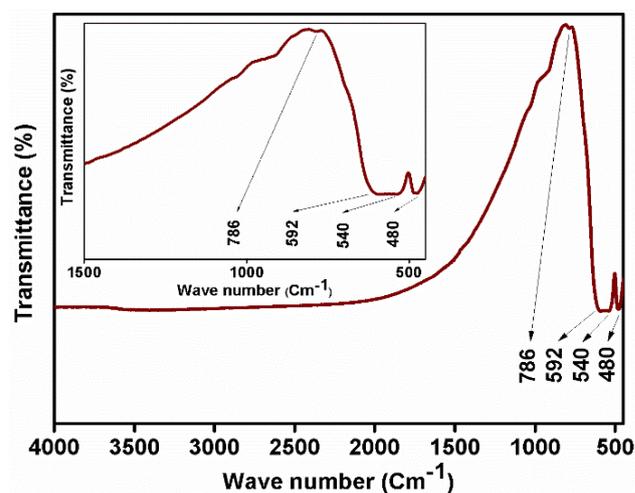


Fig. 2. FTIR spectrum of PVP assisted Fe<sub>2</sub>O<sub>3</sub> nanoparticles

### C. Scanning Electron Microscopic studies

Fig. 3 (a & b) reveals the SEM images of PVP assisted Fe<sub>2</sub>O<sub>3</sub> nanoparticles. The morphology of the Fe<sub>2</sub>O<sub>3</sub> nanoparticles shows fine particles. The absence of agglomerate reveals the effect of surfactant molecules in the preparation procedure. The particle size was found to be 100-200 nm. SEM images also show the morphologies of agglomerated particles

and surface of the nanocrystalline structures.

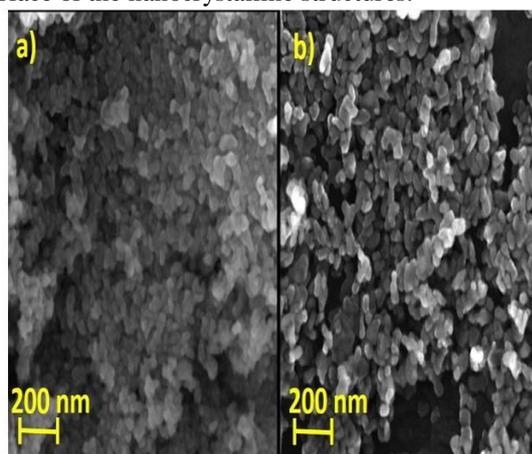


Fig. 3. SEM images of PVP assisted Fe<sub>2</sub>O<sub>3</sub> nanoparticles

#### D. Cyclic Voltammetry

The supercapacitive performance were analyzed by CV curves in aqueous 1M KOH. CV curves of the surfactant assisted hematite nanoparticles were shown in Fig. 4. The potential window was fixed between 0 to 0.5. Oxidation and reduction property of the prepared nanoparticles were analyzed through CV analysis. The CV curves were recorded for different scan rates from lower 5 mV/s to higher 100 mV/s. The anodic and cathodic peak at 0.4 V reveals the pseudocapacitive nature of the prepared material [8].

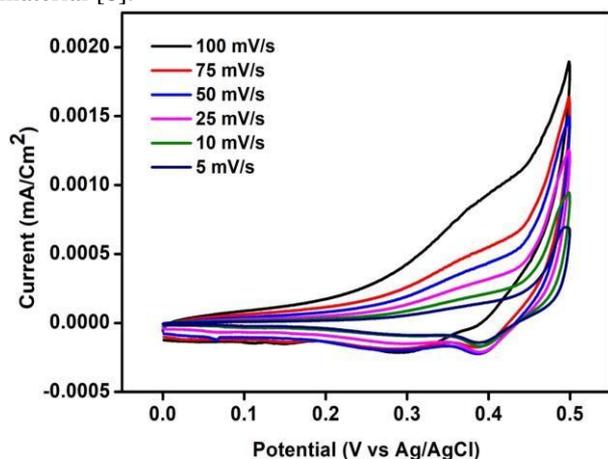


Fig. 4. CV curves of PVP assisted Fe<sub>2</sub>O<sub>3</sub> nanoparticles

#### E. Galvanostatic Charge-Discharge

The charge storage and discharge mechanism of the prepared nanoparticles were analyzed through galvanostatic charge-discharge studies. Fig. 5. shows the GCD pattern of prepared surfactant assisted hematite nanoparticles. The current density applied ranges from lower 0.2 to 0.5 mA/cm<sup>2</sup>. For very low input current the discharge is maximum as the ion transfer was very slower between the electrode and electrolyte.

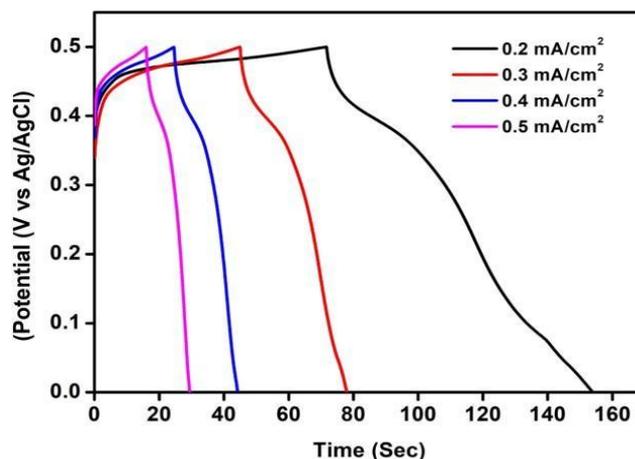


Fig. 5. GCD patterns of PVP assisted Fe<sub>2</sub>O<sub>3</sub> nanoparticles

#### F. Electrochemical Impedance Spectroscopy

The impedance, conductivity and movement of ions of the prepared surfactant assisted hematite nanoparticles were studied by electrochemical impedance spectroscopy. Fig. 6. shows the nyquist plot for the prepared nanomaterial. The frequency regions define the material supercapacitive behavior. At higher frequency region the semicircle forms which was due to the bulk resistance of the nanomaterial and at lower frequency region diffusion process takes place between ion in electrode/electrolyte interface. The small semi-circle at the beginning of the curve was due to charge transfer resistance. The slope line at almost 45° perfectly clarifies that the prepared material has supercapacitive performance.

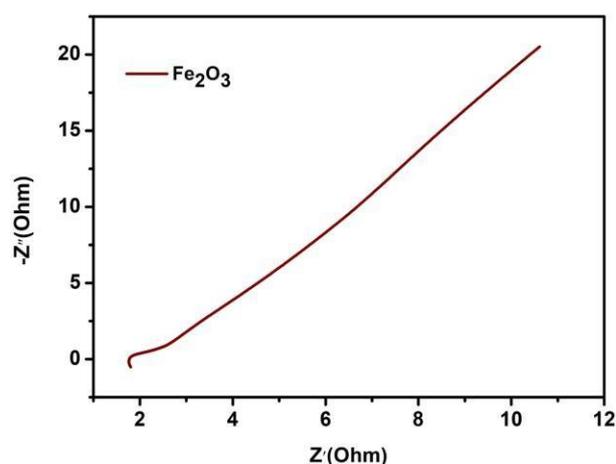


Fig. 6. EIS analysis of PVP assisted Fe<sub>2</sub>O<sub>3</sub> nanoparticles

#### IV. CONCLUSION

Iron oxide nanoparticles were prepared by chemical route. The crystallite size of the prepared nanoparticles was found to be ~ 12 nm. The XRD studies revealed that that the prepared nanoparticles have the rhombohedral structure. The SEM analyses showed that the prepared nanomaterials were in 200 nm range.

The electrochemical studies for energy storage applications revealed that the material has good redox property with excellent charge-discharge capability and also exhibits good conducting nature. Finally, it was confirmed through all the studies that the material can be used as an electrode for electrochemical storage applications.

## ACKNOWLEDGMENT

The authors show their gratitude to IRC, Kalasalingam Academy of Research and Education (KARE) for providing research facilities and owe thankful for funding under the University Research Fellowship (URF) scheme.

## REFERENCES

1. A. González, E. Goikolea, J. A. Barrena, and R. Mysyk, "Review on supercapacitors: Technologies and materials," *Renew. Sustain. Energy Rev.*, vol. 58, pp. 1189–1206, 2016.
2. X. Zhao, B. M. Sánchez, P. J. Dobson, and P. S. Grant, "The role of nanomaterials in redox-based supercapacitors for next generation energy storage devices," *Nanoscale*, vol. 3, no. 3, pp. 839–855, 2011.
3. Y.-W. Yang, T. Wang, D. Wang, J. Guo, Y. Wang, and J. Shao, "Mesoporous Transition Metal Oxides for Supercapacitors," *Nanomaterials*, vol. 5, no. 4, pp. 1667–1689, 2015.
4. E. A. Campos, D. V. B. S. Pinto, J. I. S. de Oliveira, E. da C. Mattos, and R. de C. L. Dutra, "Synthesis, characterization and applications of iron oxide nanoparticles - A short review," *J. Aerosp. Technol. Manag.*, vol. 7, no. 3, pp. 267–276, 2015.
5. Y. S. Kang, S. Risbud, J. F. Rabolt, and P. Stroeve, "Synthesis and Characterization of Nanometer-Size Fe<sub>3</sub>O<sub>4</sub> and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> Particles," *Chem. Mater.*, vol. 8, no. 9, pp. 2209–2211, 1996.
6. Q. Ma et al., "Persulfate activation by magnetic  $\Gamma$ -Fe<sub>2</sub>O<sub>3</sub> /Mn<sub>3</sub>O<sub>4</sub> nanocomposites for degradation of organic pollutants," *Sep. Purif. Technol.*, vol. 210, pp. 335–342, 2019.
7. K. Woo, H. J. Lee, J. P. Ahn, and Y. S. Park, "Sol-Gel Mediated Synthesis of Fe<sub>2</sub>O<sub>3</sub> Nanorods," *Adv. Mater.*, vol. 15, no. 20, pp. 1761–1764, 2003.
8. Z. Ma, X. Huang, S. Dou, J. Wu, and S. Wang, "One-pot synthesis of Fe<sub>2</sub>O<sub>3</sub> nanoparticles on nitrogen-doped graphene as advanced supercapacitor electrode materials," *J. Phys. Chem. C*, vol. 118, no. 31, pp. 17231–17239, 2014.
9. F. Yang, K. Xu, and J. Hu, "Construction of Co<sub>3</sub>O<sub>4</sub>@Fe<sub>2</sub>O<sub>3</sub> core-shell nanowire arrays electrode for supercapacitors," *J. Alloys Compd.*, vol. 729, pp. 1172–1176, 2017.
10. S. Yin et al., "Synergistic contributions by decreasing overpotential and enhancing charge-transfer in  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> /Mn<sub>3</sub>O<sub>4</sub> /graphene catalysts with heterostructures for photocatalytic water oxidation," *Phys. Chem. Chem. Phys.*, vol. 16, no. 23, pp. 11289–11296, 2014.
11. Y. Liu, L. Yu, Y. Hu, C. Guo, F. Zhang, and X. Wen Lou, "A magnetically separable photocatalyst based on nest-like  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/ZnO double-shelled hollow structures with enhanced photocatalytic activity," *Nanoscale*, vol. 4, no. 1, pp. 183–187, 2012.
12. B. Koo et al., "Hollow iron oxide nanoparticles for application in lithium ion batteries," *Nano Lett.*, vol. 12, no. 5, pp. 2429–2435, 2012.
13. N. Boda et al., "Effect of rare earth elements on low temperature magnetic properties of Ni and Co-ferrite nanoparticles," *J. Magn. Magn. Mater.*, vol. 473, pp. 228–235, 2019.
14. A. Abdelkader et al., "Steam reforming of ethanol over Co<sub>3</sub>O<sub>4</sub> e Fe<sub>2</sub>O<sub>3</sub> mixed oxides," *Int. J. Hydrogen Energy*, vol. 38, no. 20, pp. 8263–8275, 2013.

## AUTHORS PROFILE



**Ms. S. Ezhil Arasi** born on 1994 in Erode, Tamilnadu. She obtained her Master degree in Physics in 2017 at Bharathiar University, Coimbatore. She joined PhD in 2017 under the supervision of Dr. A. Arivarasan at Kalasalingam Academy of Research and Education in Virudhunagar district. Her research interest is focused on the area of nanomaterials and carbon-based binary metal nanocomposites synthesis for energy storage device fabrication application.

**Dr. P. Devendran** received his Ph.D degree in Physics from Madras University at Chennai in 2016, developing metal oxides and metal sulfide nano-catalysts for photocatalytic application. After he moved for postdoctoral studies at IRC, Kalasalingam academy of Research and education, he becomes an Assistant Professor of Physics at the same institution and presently began studying metal oxide modified graphene-based materials for energy storage device application and their surface science. He published more than 28 research articles and book chapters in reputed journals.



**Dr. A. Arivarasan** is currently working as Assistant Professor at Kalasalingam academy of Research and education, Virudhunagar, India. He completed his MSc (Physics) degree in Bharathidasan University, Trichy. He received both his M.Tech. (Nanotechnology) and Ph.D (Nanotechnology) degrees from Anna University in the years of 2010 and 2014, respectively on Quantum Dots for Solar Cell Applications. He has published nearly 10 publications in peer reviewed international journals and more than 25 conference proceedings. His current research interests are in the fields of supercapacitor electrodes, redox electrolytes and device fabrications.

