Structural Characterization and Dielectric Properties of Starch Coated Magnetite Nanoparticles

D. Sivakumar^{1, 2}, S. Premkumar¹, M. Madankumar¹, M Manivannan³

¹PG & Research Department of Physics, Islamiah college, Vaniyambadi -635 752, Tamilnadu, India

²Department of Physics, Sree Krishna College of Engineering, Unai, Anaicut -632 101, Tamilnadu, India

³Department of Physics, Sacred Heart College (Autonomous) Tirupattur-635601, Tamilnadu, India

⁴Department of Physics, Avinashilingam Institute for Home Science and Higher Education, Coimbatore – 641 043, Tamilnadu,

India.

ABSTRACT

The Starch coated Fe_3O_4 nanoparticles for various pH were successfully synthesized by coprecipitation method. The X-ray diffraction results showed the good crystallinity of the samples and the cubic structure of the starch coated Fe_3O_4 nanoparticle was confirmed. The functional groups were estimated by FTIR analysis. The SEM results revealed that there is no change in morphology. Dielectric behaviours of the Starch coated Fe_3O_4 nanoparticle were investigated to determine current conduction mechanisms and the development of the conductive network within the nanoparticle as a function of frequency and pH concentration. Dielectric studies show an increase in migration and polarization of mobile carriers with increase in pH. The electric modulus studies reveal the non-Debye type behavior of the sample.

Keywords: Starch, Fe₃O₄, magnetite nanoparticles, co-precipitation

1. Introduction

Nanotechnology is defined as fabrication of devices with atomic or molecular scale precision. Devices with minimum feature sizes less than 100 nanometers (nm) are considered to be products of nanotechnology. A nanometer is one billionth of a meter (10-9 m) and is the unit of length that is generally most appropriate for describing the size of single molecules. The nano scale marks the nebulous boundary between the classical and quantum mechanical worlds; thus, realization of nanotechnology promises to bring revolutionary capabilities. Fabrication of nano machines, nano electronics and other nano devices will undoubtedly solve an enormous amount of the problems faced by mankind today.

Nanotechnology is currently in a very infantile stage. However, we now have the ability to organize matter on the atomic scale and there are already numerous products available as a direct result of our rapidly increasing ability to fabricate and characterize feature sizes less than 100 nm. Mirrors that don't fog, biomimetic paint with a contact angle near 180°, gene chips and fat soluble vitamins in aqueous beverages are some of the first manifestations of nanotechnology. However, immanent breakthroughs in computer science and medicine will be where the real potential of nanotechnology will first be achieved [1].

Technology has to do with the application of scientific knowledge to the economic (profitable) production of goods and services. It is particularly concerned with the smallest devices that are possible, and equally with the appropriate laws of nanometer-scale physics: "nanophysics", which are available to accurately predict behavior of matter on this invisible scale. Physical behavior at the nanometer scale is predicted accurately by quantum mechanics, represented by Schrodinger's equation. Schrodinger's equation provides a quantitative understanding of the structure and properties of atoms. Chemical matter, molecules, and even the cells of biology, being made of atoms, are therefore, in principle, accurately described (given enough computing power) by this well tested formulation of nanophysics. There are often advantages in making devices smaller, as in modern semiconductor electronics. Any device must be composed of atoms, whose sizes are the order of 0.1nanometer. Here the word "nanotechnology" will be associated with human designed working devices in which some essential element or elements, produced in a controlled fashion, have sizes of 0.1nm to thousands of nanometers or one Angstrom to one micron [2]. There is thus an overlap with "micro technology" at the micrometer size scale. Microelectronics is the most advanced present technology, apart from biology, whose complex operating units are on a scale as small as micrometers [3].

M. Mohamed Rafi¹, K. Prem Nazeer^{1*}, A. Ayisha Begam⁴

Magnetic nanoparticles have many applications in biomedicine, such as magnetic resonance imaging contrast enhancement, cell separation, hyperthermia and drug delivery, etc [4]. These applications impose strict requirements on the physical, chemical and pharmacological properties of the nanoparticles, including chemical composition, granulometric uniformity, crystal structure, magnetic behavior, surface structure, adsorption properties, solubility as well as low toxicity. Among magnetic nanoparticles, iron oxide has gained wide attention. These nanoparticles are super-paramagnetic at room temperature; however, due to hydrophobic interactions between the particles, they agglomerate and form large clusters, resulting in an increased particle size and a low colloidal stability. In this case, the clusters exhibit strong magnetic dipole–dipole attractions and show ferromagnetic behavior [5,6]

Starch is a natural polysaccharide (made up of repeating units of glucose) and glucose is a monosaccharide. It has been used experimentally as a drug carrier because of the biocompatibility, biodegradability and nontoxity. Corboxymethylated Starch has been paid more and more attention because of its good water solubility and it is more convenient to be applied to medicine because it fits the neutral environment of the human body [7,8].

In the present study, the Starch coated Fe_3O_4 nanoparticles with different pH values have been prepared by coprecipitation method. They were systematically investigated by X-ray diffraction for crystallite size and structure. The functional groups of the prepared nanoparticles were characterized by FT-IR. The morphological characteristics of the prepared nanoparticles were studied by scanning electron microscope. The dielectric properties were studied for the different pH values.

2. MATERIALS AND METHODS

Measured weight of 1.2 g polysaccharide (Starch) was dissolved in 200 ml of distilled water and continuously stirred for 10 min at 90°C for the dissolution of polysaccharide. The solution was subsequently cooled to room temperature and aqueous solutions of FeCl₃·6H₂O (1.49g) and FeSO₄·7H₂O (0.765g) were used in the preparations. The mixed solution was then heated at 60°C under nitrogen atmosphere. Ammonia– water mix (10mol) was added drop wise to obtain a solution pH of the final mixture in the range of 8, 10 and 11. The final solution was held at 60°C for 4 h and the suspension was then centrifuged at 15,000 rpm for 10 min. The settled polysaccharide Fe₃O₄ nanoparticles were washed three times using distilled water to remove by products and excess polysaccharides. The product was again washed two times with distilled water and then with ethanol. At the end the sample was dried in an oven at 100°C for 3 hrs.

3. RESULT AND DISCUSSION

3.1 X-Ray powder diffraction analysis

In order to analyze the structure of synthesized samples, X-ray diffraction was employed using Rigaku X-ray diffractometer with CuK α (λ =1.5405Å) radiation at room temperature in the range of 5 to 80°. Figure 1 shows the XRD pattern of Starch coated Fe₃O₄ for various pH values. Characteristic peaks at 30.460°, 35.690°, 43.240°, 53.898°, 57.227° and 63.006° were observed corresponding to the (200), (311), (400), (422), (511) and (440) crystal planes of a Starch coated Fe₃O₄ with a spinal structure (JCPDS No. 85-1436). The peaks indicating that Starch coated Fe₃O₄ with a spinal structure and no characteristic peak of impurities were detected in the XRD pattern. Therefore, it was confirmed that the crystalline structure of obtained magnetite nanoparticles, agreed with the structure of an inverse spinel type oxide. The average sizes were determined from the FWHM of the XRD peaks using Debye Scherrer equation. The average grain size was calculated using the formula [9]

$$D_N = \frac{k\lambda}{\beta Cos\theta}$$

Here, D_N is the crystallite mean size, k is a shape function for which a value of 0.9 is used, λ is the wavelength of the radiation, β the full width at half maximum (FWHM) in radians in the 2 θ scale, and θ the Bragg angle. The average particle size of the Starch coated Fe₃O₄ NPs is 13nm.

The hydrophylic nature of the magnetite nanoparticle surface precludes their dispersal in water. Starch is chemisorbed on the surface of the nanoparticles, which makes the particles hydrophobic, thus these nanoparticles become dispersible in water.



Fig.1 Powder X-ray diffraction pattern of Starch coated Fe₃O₄ for various pH values 3.2 FTIR analysis

Fourier Transform Infrared spectroscopy is used to identify the functional groups and modes of vibration of the synthesized starch coated Fe_3O_4 nanoparticles using a Perkin Elmer spectrometer in the range 400-4000 cm⁻¹ with a resolution of 4 cm⁻¹. The dried sample was placed on a silicon substrate transparent to infrared, and spectra were measured according to the transmittance method. The FTIR showed a different vibration according to different functional groups which have a characteristic absorption in the IR region this give the bonds of the compounds an energy to be more stretch and curvature the peaks.

The absorptions at 1399 cm⁻¹ is a characteristic peak of the COO-Fe bond, which may be due to the reaction of hydroxide radical groups on the surface of Starch coated Fe₃O₄ [10]. The peaks at 2855 cm⁻¹ and 2924 cm⁻¹ are from the vibration of in long alkyl chain -CH₂ and -CH₃. Furthermore, the characteristic peak of -OH bond at 3378 cm⁻¹ is obviously enhanced. The peaks at 581 cm⁻¹ and 628 cm⁻¹ in confirm the existence of Fe-O bond.



Fig.2 FT-IR spectrum of the starch coated Fe₃O₄ for various pH values

3.3 SEM analysis

The morphology of the product was examined by scanning electron microscope using VEGAS3 TE SCAN and the images recorded for the samples were prepared by co-precipitation method.



Fig.3 shows the SEM images of the Starch coated Fe₃O₄ nanoparticles

Fig.3 shows the SEM images for different magnification of starch coated Fe_3O_4 and homogenous in size distribution with strong agglomeration. From the analysis, the starch coated Fe_3O_4 nanoparticles which have a spherical like particle shape with the average particle size of 10.25 nm excluding agglomerate particles, and there are some pores on the surface of the particles [11].

3.4 Dielectric analysis

Frequency dependence of the real part of dielectric constant (ϵ) of the sample is measured at room temperature using PSM 1735 N4L. The dielectric constant shows dispersion at low frequencies which is a typical character of dielectric materials. There are four types of polarization viz. (a) electronic, (b) ionic, (c) dipolar and (d) interfacial polarization, contributing to the total polarization of a dielectric material.

Interfacial polarization contributes only in the lower frequency range. The dielectric constant of the Starch coated Fe_3O_4 nanoparticles was calculated by following the relation,

$$\varepsilon = \frac{c_p d}{A\varepsilon_o}$$

Were, ε , c_p , d, A and ε_o are the dielectric constant, capacitance value, thickness, Area of the specimen under investigation and permittivity of free space (8.854×10⁻¹² F/m) respectively.

The dielectric constant of Starch coated Fe_3O_4 nanoparticles is decreases as the frequencies increases and it almost remains constant at higher frequencies. Figure 4 (a) shows the frequency dependence dielectric constant of Starch coated Fe_3O_4 as a function of frequency at room temperature. The decrease in ε' with increasing frequency may be attributed to decrease of polarization with increasing frequency before reaching a constant value when the electron hopping cannot follow the alternative field beyond a certain frequency.

The variation of dielectric loss as a function of frequency at ambient temperatures is shown in figure 4 (b). It is seen that the tan δ curve reaches a maximum at middle frequency range and then decreases at high frequencies. The tan δ vs. frequency curve exhibits a distinct relaxation which shifts towards lower frequencies as increasing pH level. At higher frequencies, however the electron-exchange between Fe³⁺ and O⁴⁻ ions cannot follow the alternation of the applied electric field. Hence tan δ fall to smaller values. The observed peak in the measured frequency region gives the relaxation peak of the material. Therefore, relaxation behavior arises whenever two phases with different electrical conductivities are in contact.



Fig.4 (a & b) Variation of dielectric constant and loss of Starch coated Fe₃O₄ as a function of frequency for various pH



Fig.4 (c) Frequency dependence real part of impedance of Starch coated Fe₃O₄ for various pH



Fig.4 (d) Frequency dependence imaginary part of impedance of Starch coated Fe₃O₄ for various pH



Fig.4 (e) Cole-Cole spectrum of Starch coated Fe₃O₄ for various pH

Complex impedance data, Z can be represented by its real, Z' and imaginary, Z". The expression of real (Z') and imaginary (Z") components of impedance related to the equivalent circuit are

$Z' = Z \cos(\theta)$ $Z'' = Z \sin(\theta)$

The variations of real Z' and imaginary part of Z'' of electrical impedance as a function of frequency for different pH are depicted in Fig.4 (c & d), respectively. The amplitude of Z' is higher in the low frequency region and it decreases monotonically with increase in frequency.

In addition, the magnitude of Z' decreases with the rise in pH. This trend of Z' may be due to increase in ac conductivity with pH and frequency. This may be due to the release of space charge polarization as a result of the lowering of the potential barrier of the materials at higher pH.

Fig.4 (e) shows the complex impedance spectra of starch coated Fe_3O_4 for some representative pH concentrations. The change in pH ensures distinct effect on the characteristics impedance spectrum of the material and these spectra show a non- ideal circle-arc that is attributed to the bulk boundary properties. The Nyquist plots of the starch coated Fe_3O_4 , as shown in Fig.4 (e) exhibited a single semicircle shape indicating the presence of polarization with a single relaxation time [12]. The radius of the semicircle represents the nanocomposite resistance, while the center of the semicircle represents the distance between nanofiller particles[13].



Fig.4 (f) Frequency dependence real part of permittivity of starch coated Fe₃O₄ for various pH



Fig.4 (g) Frequency dependence imaginary part of permittivity of starch coated Fe₃O₄ for various pH

The dielectric relaxation is described by a non-Debye model which gives the frequency dependent complex permittivity in the form: $\epsilon^* = \epsilon'$ -j ϵ'' . Where ϵ' and ϵ'' are the real and imaginary parts of the dielectric constant respectively, $j^2 = -1$.

$$\varepsilon' = \frac{Z''}{\omega c_o(Z'^2 + Z''^2)}$$
$$\varepsilon'' = \frac{Z'}{\omega c_o(Z'^2 + Z''^2)}$$

where $\omega = 2\pi f$ is the angular frequency and c_0 is the geometrical capacitance.

These relations offer wide scope for a graphical analysis of the various parameters under different conditions of pH or frequency. In Fig.4 (f) and (g) illustrate the frequency dependence of dielectric complex

permittivity (ϵ ' and ϵ ") at various pH. The dielectric constant is the ratio of the capacitance of a set of electrodes with the dielectric material between them to the capacitance of the same electrodes with vacuum between them [14].

The dielectric constant increases with the increase in pH because of the total polarization that arises from the dipole orientation and the trapped charge carrier's density due to the increase in the dissociation of ion aggregates. In fact, higher dielectric constants at low frequencies depend on ionic vibration of movement, ion–ion orientation, and space charge effects, suggest the existence of electrode polarization and space charge effects have occurred confirming non-Debye dependence. The values of ε' decreases gradually with increasing frequency and shows dispersive behavior at low frequencies. The high values of ε' , observed at low frequencies, are related to the accumulation of charges at the interface between the sample and electrodes [15].

Electric modulus

Electric modulus for determining the aspects of electrical transport phenomena of the Starch coated Fe₃O₄ was analyzed at ambient temperature. The real and imaginary parts of electric modulus were obtained from the real and imaginary parts of the measured impedance data by using the following equation,

$$M' = \frac{\omega A \varepsilon_o}{t} [Z'']$$
$$M'' = \frac{\omega A \varepsilon_o}{t} [Z']$$

The real part of the electric modulus (M') and the imaginary part of electric modulus (M'') vs. frequency plots of Starch coated Fe₃O₄ at ambient temperature for different pH are shown in Fig.5 (a & b) respectively. The observed long tail at low frequencies is attributable to the large value of electrode polarization capacitance.

For all the pH, the M' increase gradually at high frequencies and it can be observed that the electric modulus spectra exhibit overlapped peaks, which reflect the grain and grain boundary contributions. The decrease in M' value at high pH is due to the decrease of resistance of the sample and increase in electrode polarization [16,17].



Fig.5 (a) Frequency dependence real part of electric modulus of starch coated Fe₃O₄ for various pH



Fig.5 (b) Frequency dependence imaginary part of electric modulus of starch coated Fe₃O₄ for various pH

Fig.5 (b) shows the variation of imaginary part of electric modulus with frequency at selected pH. At high pH the peaks are asymmetric and broad which indicate the distribution of relaxation times. However at low pH the peaks disappeared possibly due to the frequency limitation.

The Argand plots at various pH for the Starch coated Fe_3O_4 is shown in Fig.6. The Argand plots exhibit incomplete semicircular arc, which indicates the non-Debye type relaxation process. Thus the non-Debye behavior is due to the fact that in real material there are more than one type of polarization mechanism and a lot of interactions between ions and dipoles that resulted in a distribution of relaxation time.



Fig.6 Electric modulus plots imaginary M" vs. real M' at various pH for the starch coated Fe₃O₄ nanoparticles



Fig 7 (a) Variation of resistivity of starch coated Fe₃O₄ as function of frequency for various pH



Fig 7 (b) Variation of DC conductivity of starch coated Fe₃O₄ as function of frequency for various pH

The measured value of the electrical resistivity and conductivity at various pH are shown in Fig 7 (a & b). The Starch coated Fe₃O₄ samples exhibit an increase in electrical conductivity with increase in pH. The electrical conductivity (DC) (σ) for the sample was calculated using the following relation,

$$\sigma = \frac{1}{\rho}$$

where $\rho = RA/L \sigma$ = electrical conductivity of the sample, R is the resistance of the sample, L the thickness and A the area of the sample. The electrical conductivity of starch coated Fe₃O₄ is improved with increase in the pH [18]. This improvement is due to (i) the better structural ordering that may have taken place at the higher pH. (ii) The higher concentration of the charge carriers. The resultant increase in the conduction process may be due to the reorientation of atomic sites and enhancement of short-range translational motion of charge carriers hopping with increase in frequency and pH. Lattice water and oxygen vacancies present in starch coated Fe₃O₄ NPs play a vital role in mobilizing charge carriers [19].

4. Conclusions:

The Starch coated Fe₃O₄ nanoparticles for various pH were successfully synthesized by coprecipitation method. The X-ray diffraction results showed the good crystallinity of the samples and the cubic structure of the starch coated Fe_3O_4 nanoparticle was confirmed. The average crystallite size estimated from XRD results using Scherrer formula is around 13 nm for all the samples. The functional groups were estimated by FTIR analysis. The SEM results revealed that there is no change in morphology. Dielectric behaviours of the Starch coated Fe_3O_4 nanoparticle were investigated to determine current conduction mechanisms and the development of the conductive network within the nanoparticle as a function of frequency and pH concentration. Dielectric studies show an increase in migration and polarization of mobile carriers with increase in pH. The electric modulus studies reveal the non-Debye type behavior of the sample.

REFERENCE

- 1. Cong Wang, Xudong Gao, Zhongqin Chen, Yue Chen and Haixia Chen, Polymers (2017).
- 2. Margarethe Hofmann, Brigitte von Rechenberg and Heinrich Hofmann, Nanostructured Materials for Biomedical Applications (2009).
- 3. Mahnaz Mahdavi , Mansor Bin Ahmad , Md Jelas Haron , Farideh Namvar, Behzad Nadi, Mohamad Zaki Ab Rahman and Jamileh Amin, Molecules (2013).
- 4. W.J. Deus and K. L. Caiado, Inhumas -GO, Brazil CEP 75400-000.
- 5. Wei Wu, Quanguo He, Changzhong Jiang, Nanoscale Res Lett. (2008).
- 6. Dung T.T., Danh T.M., Hoa L.T.M., Chien D.M., Duc N.H. J. of Exp. Nanosci, 4. 3 (2009).
- 7. L.M.Lacava, Z.G.Lacava, M.F.da silva, Biophys J., 80, 2483-2486 (2001).
- 8. Y.Zhang, N.Kohler and M.Zhang, Biomaterials 23, 1553-1561 (2002).
- 9. Javier A. Lopez, Ferney González, Flavio A. Bonilla, Gustavo Zambrano, Maria E. Gómez, Rev. LatinAm. Metal. Mat. 30 (1), 60-66 (2010).
- R.Y.Hong, S.Z.Zhang, G.Q.Di, H.Z.Li, Y.Zheng, J.Dinge, D.G.Weif, Mater Res Bull 43, 2457-2468 (2008).
- 11. JingxingYang, XuweiYang, HuaYang, J. alloy. compounds. 512, 190-194 (2012).
- 12. Deng Xu V. Sridhar S. P. Mahapatra Jin Kuk Kim, J. Appl. Poly. Sci. 111, 1358–1368 (2009).
- 13. B P Sahoo, K Naskar, A Dubey, Ram N. P. Choudhary, D K Tripathy, J. Mater. Sci. 48 702–713 (2013).
- 14. Mohammed H Al-Saleh, Haya K Al-Anid, Yazan A Husain, Hasan M El-Ghanem and Saadi Abdul Jawad, J. Phys. D: Appl. Phys. 46, 385305 (2013).
- 15. A. Karmakar, A. Ghosh, Current Applied Physics 12, 539-543 (2012).
- 16. Shujahadeen B. Aziz, Adv. Mater Sci. Eng., 2527013, 1-11 (2016).
- 17. B.Nageswara Rao, O.Padmaraj, D.Narsimulu, M.Venkateswarlu, N.Satyanarayana, Ceramics Int. Part B, 41(10) 14070-14077 (2015).
- 18. S. Kalaiarasi, M. Jose, Appl. Phys. A 123:512 1-10 (2017).
- 19. D. Siva Kumar, M. Chandra Babu Naidu, M. Mohamed Rafi, K. Prem Nazeer, A. Ayisha Begam, G. Ramesh Kumar. Materials Science-Poland, 36(1), 123-133 (2018).