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Research Paper

Preparation and Characterization of Zinc doped Magnetite Nanoparticles using Green Synthesis

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Abstract: *Zinc doped Nanomagnetite was synthesized in lab by biological method using plant extract as it does not involve any harmful chemicals and are ecofriendly in nature. In the present work, zinc doped magnetite nanoparticles were synthesized using completely green synthesis by chemical route method. The band- gap of the zinc doped Fe_3O_4-NPs was investigated by UV-Vis Absorption Spectroscopy, grain size is calculated using XRD and its energy shifting was studied by FTIR , also its conductivity (i.e. the ability or power to conduct or transmit heat, electricity, or sound) was measured by TDS Conductivity meter. The doped nanoparticles synthesized through this green method can potentially useful in various biomedical applications*.

Keywords: Nanomagnetite, precipitation method, UV-Vis Absorption Spectroscopy, FTIR, XRD, conductivity, nanoparticles.

Introduction

Magnetite (Fe_3O_4), is a natural iron oxide magnet, has a distinctive characteristic. Magnetite is the most magnetic of all the minerals on Earth. It has an inverse spinel structure with oxygen, forming a face-centered cubic crystal system. In magnetite, all tetrahedral sites are occupied by Fe^{3+} and octahedral sites are occupied by both Fe^{3+} and Fe^{2+}. Magnetite is a versatile material because of its physical-chemical properties such as mechanical, electrical, optical, magnetic properties [1-4]. It is used in various applications like high gradient magnetic separation, magnetic resonance technology, drug delivery and various biomedical fields [5-7].

Magnetic properties of magnetic nanoparticles can be tailored by their particle sizes and size distributions. The particle sizes and size distributions of magnetic nanoparticles are, in turn, affected by the synthesis route. For these reasons, various synthesis approaches have been developed to produce Fe_3O_4 nanoparticles in order to obtain desired properties [8-11].

After many research works, it has been proved that the magnetite nanoparticles concert can be improved further by doping. The synthesis of magnetite in the presence of divalent and trivalent cations of transition metals (viz V^{3+},Zn^{2+},Cr^{3+},Mn^{2+},Co^{2+},Ni^{2+},Li^{2+}) can modify electrical, magnetic, structural, optical, saturation magnetization properties of iron oxide[12-14]. All these properties are helpful in understanding the mechanism of formation of rust in alloy elements and also help to understand the factors which influence magnetism change because of impurities better.

As magnetite nanoparticles consist of a defensive coating and a magnetic core with active surface functionality, so that biomolecules can easily get attached to the surface of nanoparticle[15-17]. And this property can be widely used in many scientific applications.

Zinc belongs to the microelements group/category that can play a vital role in many important biochemical reactions and physiological processes, such as development and growth of cells [18].

Different types of synthesis techniques are used for the synthesis of zinc-doped magnetite nanomaterials such as bottom-up approach, viz sol-gel technique, chemical precipitation technique and in top-down, ball milling etc.

Recently, great efforts were made to use green and ecofriendly method for synthesis of nanosize materials. These efforts include the use of plant or fruit extracts as surfactant [19,20]. Parts of plants such as a leaf, latex, stem, seed, and root are being widely used for nanoparticle synthesis [21]. The greener & environment friendly processes are becoming very much popular, for preparing nanoparticle using naturally occurring reagents, which would be an attractive feature in the field of nanotechnology. The precipitation method using green synthesis is an ecological technique gives high quality, zinc doped nano powder. In the present study characterization of zinc-doped magnetite nanoparticle has been done by UV-VIS spectroscopy, XRD & FTIR technique.

Material and Methods

Green Synthesis Precipitation Method

In our work, Zinc doped Magnetite nanoparticles were synthesized using green synthesis ecofriendly approach. Aqueous solution of ferrous sulphate, Zinc acetate dehydrate and ferric chloride solution prepared in plant extract is precipitated in 2:1:1 ratio(i.e.0.4 M of $FeSO_4$ {prepared in leaf extract solution} is mixed with 0.2M $Zn(CH_3COO)_2$ solution, stir the solution well simultaneously with constant stirring , add 0.2 M of $FeCl_3$ solution to the mixture). After 10 mins. Of constant stirring the solution is mixed with 0.1 M NaOH. This reaction mixture is kept at 85-90^{0}C for 4 hours. Then zinc doped magnetite nanoparticles were magnetically collected. All chemicals used were of analytic grade.

The above process is being given below in form of flow chart:

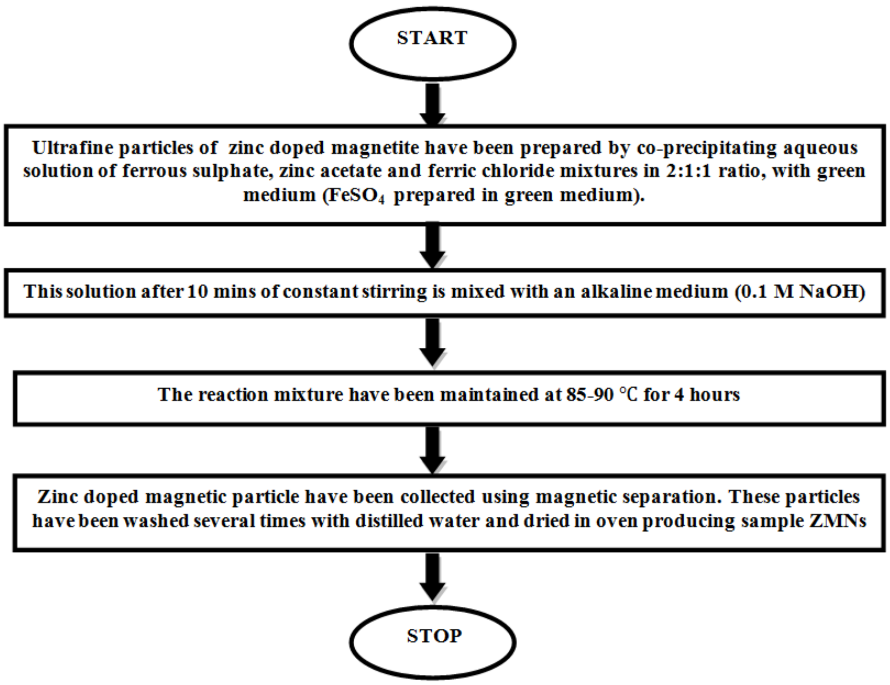


Figure 1: Flow chart for preparation of Zinc dopped magnetite nanoparticles

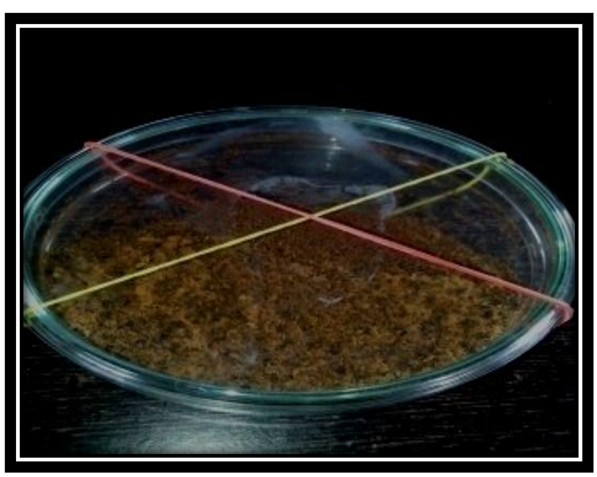


Figure 2: Zinc doped magnetite nanoparticles

Characterization

UV-Vis absorption is first characterization technique for prepared nanoparticles, to check whether the prepared sample is in nano range or not as it gives information about formation of nanoparicles, the band-gap, and its size distribution, from the absorption spectrum.

The optical absorption of Zinc doped magnetite nanoparticle of which is measured in a scanning range of wavelength from 300 to 800 nm, with scan interval of 5nm as shown in figure,. By the optical absorption result, it is possible to determine band gap of prepared sample.

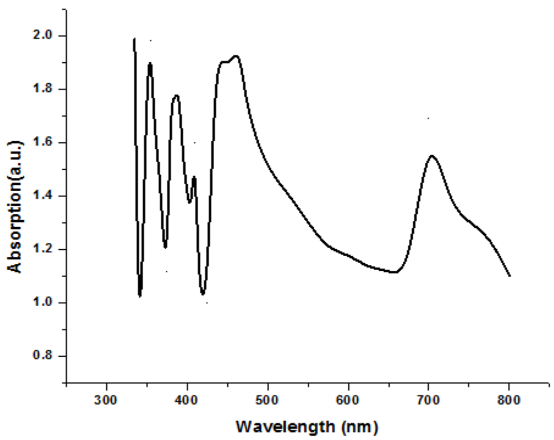


Figure 2: Absorbance spectrum of zinc doped magnetite nanoparticles

The absorbance peak is related to the band gap energy, and hence using maximum absorbed wavelength, we can convert peak wavelength into band-gap energy. This can be converted by using famous Einstein-plank's relation:

$$E = \frac{hc}{\lambda}$$

Where,
E = band gap energy,
h = plank constant,
c = velocity of light,
λ = maximum absorbed wavelength.
By putting the respective values in above equation,

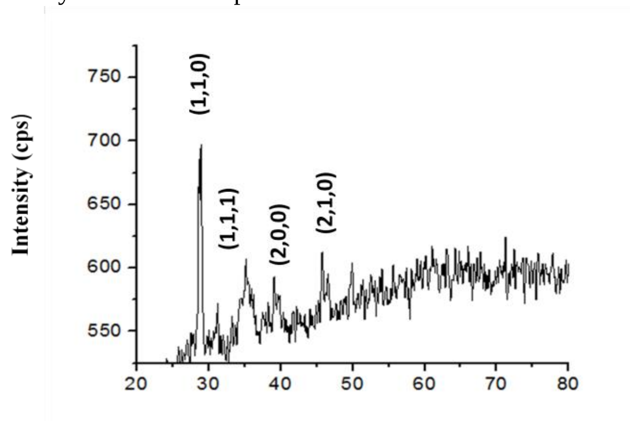
$$E = \frac{1241}{490} eV$$

We obtained band gap energy ~2.49 eV, and its absorption edge occurs at about λ= 490 nm.

X-Ray Diffraction

X-ray diffraction is a swift technique used for phase identification of a crystalline material and can provide information on unit cell dimensions. Powder diffraction is often easier and more expedient/convenient than other crystal diffraction.

In powder XRD, the sample is usually in a powdery form, consisting of fine grains of crystalline material to be studied. Here we have used Brucker D-8 Diffractomter, which measures data in transmission mode, and is used mostly with solid sample.



2θ (°)

Figure 3: XRD graph of zinc-doped magnetite nanoparticle

The zinc-doped magnetite naoparticles were grown in polycrystalline nature, as there are number of XRD peaks endorsed/attributed to different crystalline orientation.

Fourier Transform Infrared (FTIR) Spectroscopy

It is a measurement technique for collecting infrared spectra. It is also cheaper than other conventional spectrometers, as a single spectrum measurement is faster than multiple one because it measures information at all frequencies simultaneously.
An infrared spectrum shown in graph is obtained by passing IR radiation through the pallet sample, which determines that fraction of incident radiation is absorbed maximum at particular energy.

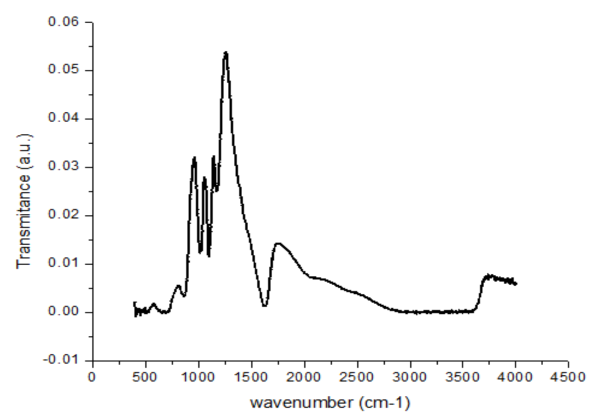


Figure 4: FTIR spectrum of zinc-doped magnetite nanoparticle

The shifting happening at wavelength range of 1500-4000 cm^{-1} is clearly recognizable and the maximum absorption occurred at 1500-1750 cm^{-1} of range. (Figure 4).

Results and Discussion

UV-Vis Spectroscopy

The UV-Vis spectroscopy revealed that the material has turned into nanoparticle form, showing enhancement in band gap to ~2.49 eV, this absorption edge occurs at about 490 nm, optical studies revealed that band gap of zinc-doped magnetite nanoparticles is higher than pure Fe_3O_4[22]

Theoretical Calculation

For determining particle size**,** Effective Approximation Method formula is used, the formula is given below[23/14]:

$$E = E_g + \frac{\hbar^2 \pi^2}{2R^2}\left\{\frac{1}{m_e*} + \frac{1}{m_h*}\right\} - \frac{1.8e^2}{4\pi\varepsilon R}$$

Where,
E = band gap of the synthesized particle,
Eg = bulk band gap (0.1 eV),
R = radius of the particle,
m_e* = effective mass of electron (100m),
m_h*= effective mass of hole(100m),
m = mass of electron,
ε is dielectric constant of the material.
On putting the respective values, in above equation:

➡

$$E\text{-}Eg = \frac{(1.054 * 10^{-34})^2 * 3.14^2}{2 * R^2 * (10^{-18})}$$

$$\left\{\frac{1}{100 * 9.1 * 10^{-31}} + \frac{1}{100 * 9.1 * 10^{-31}}\right\} - \frac{1.8 * (1.6 * 10^{-19})^2}{\varepsilon * R * 10^{-9}}$$

➡

$$2.39 = \frac{1.0964 * 10^{-49}}{R^2}$$

$$\{2.197 * 10^{28}\} - \frac{5.4211 * 10^{-30}}{R}$$

➡

$$2.39R^2 + 2.45\times10^{-29}R - 1.208 = 0$$

Solving above quadratic equation, the value of R came to be 1.11 nm, which give particle size ~ 2nm.

Conductivity Measurement

The conductivity measured, using TDS Conductivity meter is came to be 0.01 milli-Siemen.

XRD Measurement

The XRD data is used in interpretation of grain size of crystal using Scherror formula

$$t = \frac{0.9\lambda}{B\cos\theta}$$

Where t is the particle size, λ is the wavelength of the incident X-ray beam, θ is the Bragg's diffraction angle, B is Full width at half maxima (FWHM) of the Zn doped magnetite peak.

The calculated size of nanocrystallites with the Scherrer formula was in the range of 11.9 **-** 15.03 nm.

FTIR Spectroscopy

The FTIR spectrum shows presence of absorption bands at 1645 cm^{-1} associated with Fe-O stretching vibrations of Fe^{2+} and Fe^{3+} ions confirm Fe_3O_4 inverse spinel structure formation [22].

Conclusion

The green synthesis is used for the zinc doped nanomagnetite preparation has become an advance and new technique reveals that , the synthesized nanoparticles are in nanorange, interpreted using XRD, FTIR & Uv-Vis spectroscopy , which are conductive in nature.

Aknowledgement

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