

Synthesis and Characterization of PVP Coated Fe_3O_4 Magnetic Nanoparticle Prepared at Low Temperatures

M.Gurumoorthy¹, M.Anbarasu,¹K.Parasuraman¹, K.Samuvel² and K.Ramachandra²

¹ Department Of Physics, Poompuhar College (Autonomous), Melaiyur 609107, Tamilnadu
gurumoorthy8@gmail.com

² Department of Physics, SRM University, Vadapalani Campus, Chennai 600026, Tamilnadu
Corresponding author phone no. +91 9842638755

Abstract— In this paper focuses on polyvinylpyrrolidone (PVP) functionalized Fe_3O_4 /PVP magnetic nanoparticles (MNPs) are prepared by solid-state reaction method. Hexamethylenediamine ($C_6H_{16}N_2$) is used as a precipitating agent and a base. It observes that temperature influences the response procedure for the formation of Fe_3O_4 /PVP magnetic nanoparticles. The nanoparticles are collected and characterized by X-ray diffraction (XRD), Laser Raman spectroscopy (LRS), Ultraviolet visible spectrometer (UV-Vis), Energy dispersive spectroscopy (EDS), Field emission scanning electron microscopy (FE-SEM). Their magnetic property is analyzed via vibrating sample magnetometer (VSM).

Keywords— Fe_3O_4 nanoparticles, polyvinylpyrrolidone, temperature, solid state reaction.

1. INTRODUCTION

Fe_3O_4 nanomaterials are a critical reputation for their chemical and physical properties. Since they are adjusting the stature and structure of metal oxides [1-3]. These nanomaterials have gathered plenty of priority featuring in numerous fields such as hyperthermic treatments [4], magnetic resonance imaging [5], drug and gene delivery [6], water treatment [7], and recoverable catalyst [8]. sensor [9] proton exchanged membrane [10] optoelectronic devices [11], cell separation [12], and magnetic bio-separations [13].

Magnetite (Fe_3O_4) is permanently bringing huge awareness and it has a superior biocompatibility, gigantic moment at under magnetic field, superparamagnetic character, solidity and lesser cytotoxicity [14-18]. Magnetite nanoparticles could cause noxious reaction to the human anatomy before bio-medicine treatment. For instance, when ferrous ions have been suspected in formation of responsive oxygen group. They can make complete blemish on deoxyribonucleic acid, proteins or fatty acid particles [19-22]. Hence, peoples are regularly consume specific surfactants or polymer to adjust the magnetite nanoparticles to recover their colloidal stability in physical conditions and diminish harmfulness [23,24].

Polymer system has a temperament in the preceding years to generate combinations of various polymers in place of creating different polymers. The intermixture of polymer is one of the straightforward to achieve a collection of physical and chemical properties from the ingredient of polymers. The compatibility or miscibility of the polymers are improved in unfamiliar condition. Compatibility is making the capability of two or numerous polymer materials to blend together. Miscibility is capacity to develop a particular phase over absolute ranges of temperature, pressure, and composition. The miscibility period illustrates the homogeneity of polymer blends at specific temperatures. Miscibility can be determined over several aspects such as morphology, crystalline phase, intermolecular interaction, and reduction of surface tension.

Polyvinylpyrrolidone (PVP) has huge dielectric constant, resistance, stability, compatibility, dissolubility and massive scale screen production. PVP finds excellent use for life-saving substances such as blood plasma. An appropriate solution to a concentration of 3.5 percentages of the polymer can be used as a substitute for blood plasma. This solution is very stable over a long period of time and can be gives to patients, irrespective of their blood groups. PVP polymer dissolves in ketones, ethers, chlorinated hydrocarbons and alcohol. It is generally resistant to attack by many strong chemicals and good substitute for materials such as asbestos and mica. The applications of PVP are suspending mediator, coating agent, tablet binder and hydrophilizing biomaterial [25,26]. The superficial effects of PVP are essential in various functions as they generally demonstrate the surface appearance of medicinal gillings, mucosa and synthetic organs [27].

Several procedures are being involved to developing PVP coated Fe_3O_4 nanoparticles. They are thermal disintegration of natural iron precursor [28], sonochemical technique [29], nonaqueous approach [30], microemulsion route [31], chemical coprecipitation method [32], hydrothermal synthesis [33], etc. [34]. These techniques are identified as relatively easy, but need a many processes. The processes are decomposition of metallic precursor and surfactant elements in a solvent along large boiling point, composing of metal-surfactant complicates etc [35]. It needs a high amount of organic solvent including lesser solubility and acceptable environment [36] and financial issue [37] in removal of solvent.

To overcome the particular trouble, in this paper, we are describing a solid state reaction method to combine Fe_3O_4 nanoparticles. Its size can be efficiently under control using mixing and steaming of metallic salt and surfactant elements.

That is commonly used approach during composite of many crystalline manganites. This approach gives a massive choice of action based on oxides, carbonates, etc. Because hard materials are not responding to one another on normal temperature (NT). It's essential to increase higher temperatures for the suitable reaction to arriving at considerable proportion. Advantage of using this

method is lower reaction, possibly stabilize metastable phases, eliminate intermediate impurity phases, produce products of small crystallites/high surface area.

In this activity PVP coated Fe_3O_4 magnetic nanoparticles are synthesized by solid-state reaction method at various temperatures. It observes that temperature influences the response procedure for the formation of Fe_3O_4 /Pvp magnetic nanoparticles. The samples are characterized by X-ray diffraction (XRD), Laser Raman spectroscopy (LRS), Ultraviolet visible spectrometer (UV-Vis), Energy dispersive spectroscopy (EDS), Field emission scanning electron microscopy (FE-SEM) and vibrating sample magnetometer (VSM).

II. MATERIALS AND METHODS

2.1. MATERIALS

Iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), iron (II) chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), hexamethylenediamine ($\text{C}_6\text{H}_{16}\text{N}_2$) and polyvinylpyrrolidone ($\text{C}_6\text{H}_9\text{NO}$)_n are purchased from sigma Aldrich company India.

2.2. SYNTHESIS OF Fe_3O_4 NANOPARTICLES

Fe_3O_4 nanoparticles are prepared by solid-state reaction method. Iron (III) chloride hexahydrate, iron (II) chloride tetrahydrate and hexamethylenediamine are ground individually by using agate mortar. Then, suitable quantity of Iron (III) chloride hexahydrate, iron (II) chloride tetrahydrate and hexamethylenediamine powders are blended together and ground completely.

2.3. Coating of PVP on Fe_3O_4

The suitable amount of Fe_3O_4 nanoparticles and polyvinylpyrrolidone are mixed together and ground thoroughly. Finally, the powder is heated in a muffle furnace for 3h at 200°C and 500°C designated as A and B samples respectively.

III. RESULTS AND DISCUSSION

Figure 1 shows the XRD pattern of PVP coated Fe_3O_4 nanoparticles at different temperatures. XRD pattern is recorded the crystal formation of Fe_3O_4 /PVP nanoparticles. It is created (sample A) complete reflection peaks are nominated to diffraction at (220), (311), (222), (400), (331), (422), (511), (440) planes of cubic phase of Fe_3O_4 (space group : Fd-3m) which is nearly to the observation principles (JCPDS card no. 65-3107). And in (sample B) all the reflection peaks are nominated to diffraction from (220), (311), (400), (331), (422), (440), (531), (533) planes of cubic arrangement of Fe_3O_4 (space group : Fd-3m) which is nearly to the observation values (JCPDS card no. 82-1533). It is pointed out PVP coated Fe_3O_4 nanoparticles by a solid-state reaction method at different temperatures. That is noticed the strength of each diffraction peak of Fe_3O_4 nanoparticles unsteady which indicated due to coating from PVP in Fe_3O_4 nanoparticles.

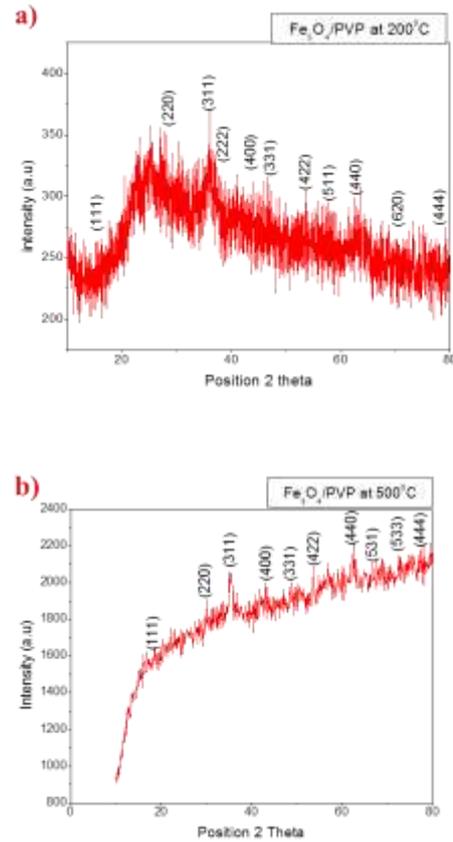


Fig.1. XRD patterns of PVP coated Fe_3O_4 nanoparticles (a) at 200°C (b) at 500°C

The typical grain volume of nanoparticles calculated from Scherrer equation:

$$L = k\lambda / \beta \cos\theta \quad [38].$$

Where L is element diameter, k is constant, λ is X-ray wavelength, β is the full width half maximum and θ is diffraction angle. The particle size is measured from FWHM of the high intense peak using Debye-Scherrer formula. The crystallite size is calculated to sample A 11nm and to Sample B 25 nm respectively. The reaction temperature is increased grain size and intensity. The peaks are becoming broad,

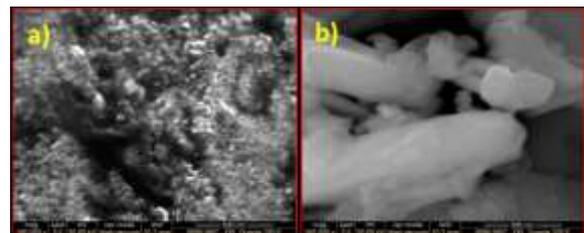


Fig.2. FE-SEM image of PVP coated Fe_3O_4 nanoparticles (a) at 200°C (b) at 500°C

The FE-SEM image of PVP coated Fe_3O_4 at 200°C sample (A) is shown in Fig. 2a. The Fe_3O_4 /PVP nanoparticles are accumulated and stuck tight together. Its huge efficiency created the time between a start of

mechanical progress. Lack of acute peaks are in the XRD pattern proves the presence of small particles to form chainlike structure. FE-SEM describes that the samples exist for aggregation of lesser particles at a magnification of 5000 times the presence of large dense, agglomeration reveals that pore free crystallites are available on the surface.

Fig.(2b) shows SEM micrographs of PVP coated Fe₃O₄ nanoparticles at 500°C of sample (B). This measures that PVP decreases the agglomeration of the nanoparticles. It is evident that the existence of PVP very much influences the crystallite size, dissemination and diffusion of the appearing nanoparticles. Consistent nanoparticles with near size distribution and sphere shapes with weak agglomeration are acquired for PVP coated samples . It is clear that particles are of spherical shape and are agglomerated. From XRD pattern , we can find that most of the coated nanoparticles average size around 11nm and 25 nm respectively.

The EDAX spectra are used for measurable constituent investigation of PVP coated Fe₃O₄ nanoparticles prepared at different temperatures, shown in Fig. 3 (a) and (b) properly. The equivalent peaks in sample A (at 200°C Fe₃O₄/PVP nanoparticles) and Sample B (at 500°C Fe₃O₄/PVP nanoparticles) are due to Fe and O. PVP coated nanoparticles shows additional peaks equivalent of C as expected. Both the spectra do not display any extra impurity peak indicating the purity of samples. The analysis of elements details is given in Table 1.

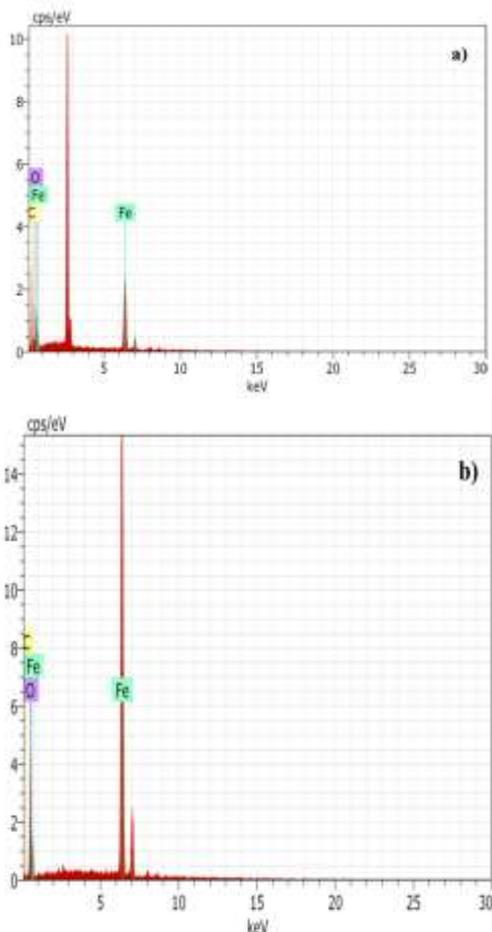


Fig.3. EDAX image of PVP coated Fe₃O₄ nanoparticles (a) at 200°C (b) at 500°C

Table 1

Elemental analysis for both samples (A and B) PVP coated Fe₃O₄ MNPs at different temperatures.

Elements	At%	
	Fe ₃ O ₄ /PVP at 200°C (A)	Fe ₃ O ₄ /PVP at 500°C (B)
Fe	3.88	35.08
O	34.66	51.90
C – PVP	61.46	13.02

Optical absorption spectrum of magnetite nanoparticles are shows an absorption band in the region 330-1960 nm, proves that the powerful UV absorption of the material. The absorption peaks are observed to be switched slightly approaches wavelength to Hypsochromic shift (blue shift) at 328 nm in sample A and 343nm in sample B respectively. The value (~329.5 nm) is closed with a previous literature [39]. The absorption peaks are observed to slightly reaches wavelength to Bathochromic shift (red shift) at 558 nm in sample A and 530nm in sample B respectively. The appearance of various absorption peaks shows Hypochromic and Hyperchromic shift in sample A and sample B respectively. In sample B Characteristic Absorption peaks are broadened when increasing the reaction temperature of PVP coated Fe₃O₄ nanoparticles.

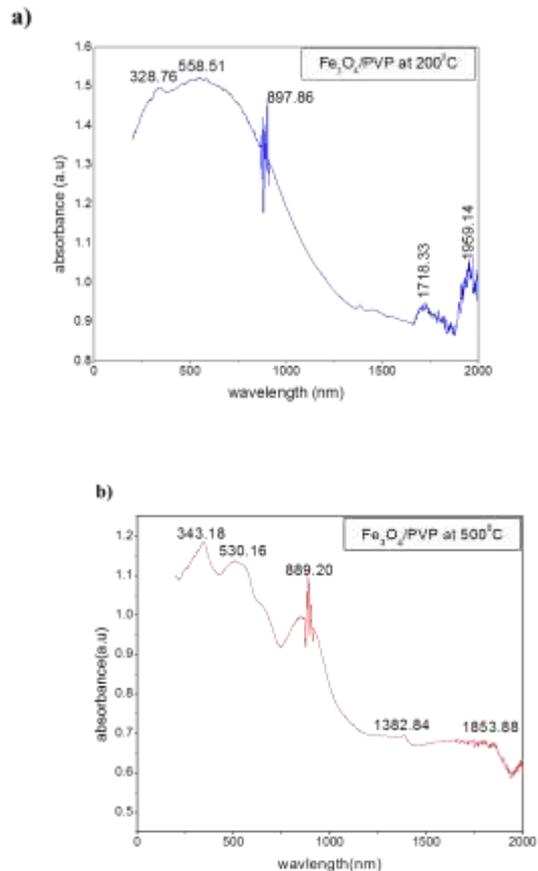


Fig.4. UV spectrum of PVP coated Fe₃O₄ nanoparticles (a) at 200°C (b) at 500°C

The visual band gap intensity has been computed utilizing the Tauc relation [40].

$$ah\nu = A(h\nu - E_g)^m$$

Where a is absorption coefficient and is known by $a = 2.303 \log (T/d)$ (d is thickness and T is a transmission), $h\nu$ is the photon energy, A is a constant, E_g is the band gap of a substance and m for various values respecting direct/indirect band gap. Fig.5 views the $(ah\nu)^2$ against $h\nu$ graph of PVP coated Fe_3O_4 nanoparticles. The band gap (E_g) values of the material have been approximated by catching the interrupt of the projection to lowest point absorption with photon energy axis. The optical band gaps of the PVP coated Fe_3O_4 nanoparticles have been computed and are established to be 2.83 and 2.53 eV for (at 200°C and 500°C) respectively. The band gap energy is decreased due to increase of the substance temperature on PVP coated Fe_3O_4 nanoparticles. Fe_3O_4 nanoparticles show a decrease in energy gap matching along bulk Fe_3O_4 (3.0 eV) due to a coating of PVP and temperature.

Still, the as-synthesized substance has a band gap lesser than the bulk one. This result is expected because of chemical imperfection or vacancies available in intergranular attacks and metallurgy is created different intensity level to decrease the band gap energy. The band gap of the Fe_3O_4 nanoparticles is nearby to the article reported value (0-3.0 eV)[41].

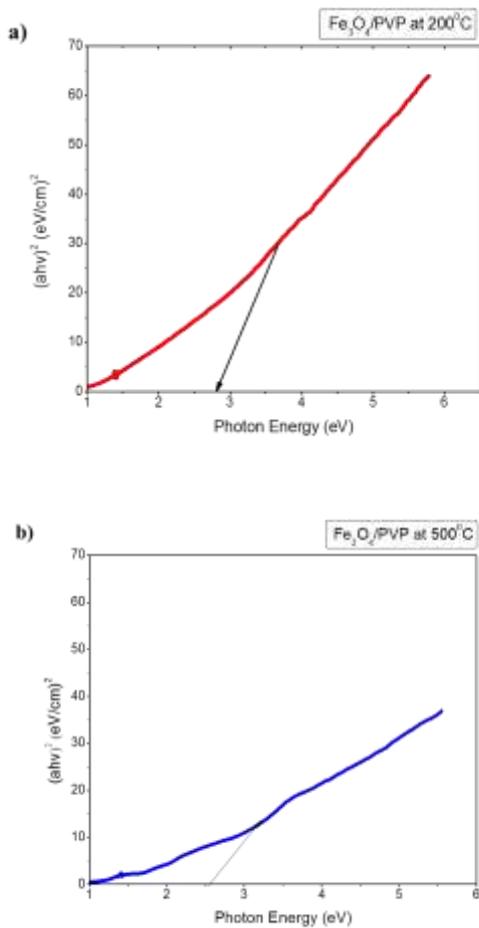


Fig.5. Band gap energy calculation graph of PVP coated Fe_3O_4 nanoparticles (a) at 200°C (b) at 500°C

Figure 6 shows Raman spectra of PVP coated Fe_3O_4 nanoparticles at different temperatures. The weak peaks are observed around 198cm^{-1} and 446cm^{-1} , because of PVP coated Fe_3O_4 nanoparticles at lower temperature (at 200°C). The peak is around 446cm^{-1} approaches to the T_{2g} mode bending of oxygen with consideration to Fe. Five vibration modes are viewed in sample B. The peak is nearly at 617cm^{-1} assigned to A_{1g} mode (symmetric stretch of oxygen atoms along Fe-O bond) and generally is connected to structural properties. The peaks are around 300cm^{-1} to 500cm^{-1} attribute to the T_{2g} mode (symmetric and asymmetric turning of oxygen with respect to Fe) and they are combined with electronic properties[42]. At higher peaks are in the range of $1300\text{-}1400\text{cm}^{-1}$ because of the formation of $FeOOH$, $\alpha\text{-}Fe_2O_3$, $\gamma\text{-}Fe_2O_3$ phases[43].

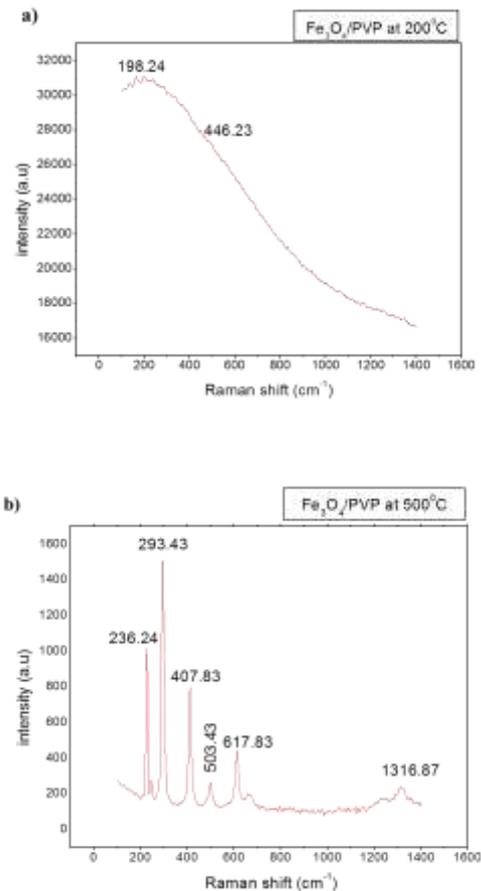


Fig.6.

Laser Raman spectra of PVP coated Fe_3O_4 nanoparticles (a) at 200°C (b) at 500°C

The figure 7 shows M-H curve of PVP coated Fe_3O_4 nanoparticles at different temperatures. Saturation magnetization (M_s), remanence magnetization (M_r), Coercivity (H_c) and squareness ratio (M_s/M_r) values are tabulated in Table 2. The saturation magnetization (M_s) of Fe_3O_4/PVP sample is increased to an increase in reaction temperature of nanoparticles. It can be noticed that the lesser particle sizes show lesser values of M_s , due to the surface middle and changed cationic allocation[44]. The decrease in saturation magnetization at smaller sizes is credited to appreciable surface effects in these nanoparticles.

Magnetic Saturation (M_s) of magnetic polymers are usually in the region of 4-30 emu/g [45-49]. The polymer is effect coating and encapsulation the Fe_3O_4 nanoparticles and decreased the M_s value. This result is due to the existence of the diamagnetic mechanism and reduction of magnetite ratio in every colliding. [50]. Each sample is shown superparamagnetic nature and has smaller saturation magnetization values than the bulk Fe_3O_4 [51]. The saturation magnetization of the elements is equivalent to its volume[52]. Since developed Fe_3O_4 illustrate the lesser M_s .

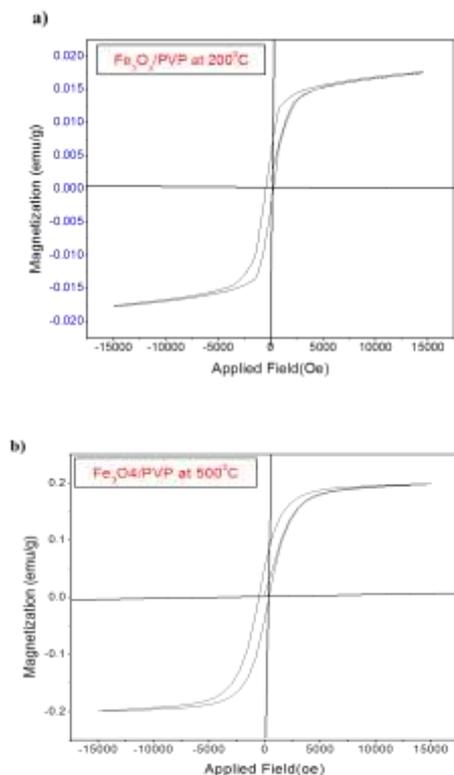


Fig.7. M-H curves of PVP coated Fe_3O_4 nanoparticles (a) at $200^\circ C$ (b) at $500^\circ C$

Table 2

Saturation magnetization (M_s), remanence magnetization (M_r), Coercivity and squareness ratio (M_s/M_r) values are calculated from the M-H curves for Fe_3O_4/PVP at $200^\circ C$ (sample A) and Fe_3O_4/PVP at $500^\circ C$ (sample B).

	Fe_3O_4/PVP at $200^\circ C$ (A)	Fe_3O_4/PVP at $500^\circ C$ (B)
M_s(emu/g)	17.61	40.02
M_r(emu/g)	4.98	9.94
Hc (oe)	364.86	442.73
M_r/M_s	0.28	0.24

IV. CONCLUSION

In summary, PVP coated Fe_3O_4 nanoparticles are groomed by solid-state reaction method at low temperatures. PVP added to synthesize system, the morphology becomes small particles at $200^\circ C$ and spherical structure at $500^\circ C$ respectively. As a result, diameter size is around in the range of 11 nm - 25 nm. The PVP coated Fe_3O_4 nanoparticles are

exhibited super-paramagnetic behavior at room temperature. The Optical band gap is in the region between 2.53 – 2.83 eV and Laser Raman spectroscopy shows good absorption peaks and EDAX shows all the elements present in the sample.

ACKNOWLEDGMENT

The author would like to express his thanks to the University Grants Commission, South Eastern Region (UGC-SERO), Hyderabad, India, for sanctioning the financial assistance [F.No. 6304/15 Dated:] to carry out the the present research work.

REFERENCES

- [1] Wang B, Chen JS, Wu HB, Wang ZY, Lou XW. J Am Chem Soc 2011; 133: 17146– 8.
- [2] Wei ZH, Zhou ZJ, Yang M, Lin CH, Zhao ZH, Huang DT, et al. J Matter Chem 2011; 21:16344 – 8.
- [3] Wang Y, Liao ZL, She GW, Mu LX, Chen DM, Shi WS. Appl Phys Lett 2011;98:203108–10.
- [4] Bai LZ, Zhao DL, Xu Y, Zhang JM, Gao YL, Zhao LY, et al. Mater Lett 2012;68:399–401.
- [5] Tan H, Xue JM, Shuter B, Li X, Wang J. Adv Funct Mater 2010;20:722–31.
- [6] Veisheh O, Gunn JW, Zhang MQ, Adv Drug Deliv Rev 2010;62:284–304.
- [7] Li XY, Si ZJ, Lei YQ, Li XN, Tang JK, Song SY, et al. Cryst Eng Commun 2011;13:642–8.
- [8] Zeng TQ, Chen WW, Cirtiu CM, Moores A, Song GH, Li CJ. Green Chem 2010;12:570–3.
- [9] Y.L. Luo, L.H. Fan, F.Xu, Y.S. Chen, C.H. Zhang, Q.B. Wei, Mater.Chem.Phys.120(2010)590– 597.
- [10] Z.Ma, H.Liu, Particuology 5 (2007) 1– 10.
- [11] T.Muraliganth, A.V.Murugan and A.Manthiram, Chem.Commun.,2009,7360–7362.
- [12] S.Xuan, L. Hao, W.Jiang, X.Gong, Y.Hu and Z. Chen, Nanotechnology, 2007, 18, 035602.
- [13] I.J. Bruce, T.Sen, Langmuir 21 (2005) 7029.
- [14] Y.H. Deng, D.Qi, C.H. Deng, X.M. Zhang, D.Y.Zhao. J.Am.Chem.Soc. 130 (2008) 28– 29.
- [15] X.Xu, C.Deng, M.Gao, W.Yu, P.Yang, X.Zhang. Adv. Mater. 18 (2006) 3289– 3293.
- [16] J.Park, K.An, Y.Hwang, J.G.Park, H.J.Noh, J.Y. Kim, J.H. Park, N.M.Hwang, T.Hyeon Nat.Mater.3 (2004) 891– 895.
- [17] K.Mori, Y.Kondo, S.Morimoto, H.Yamashita. J.Phys.Chem.C 112 (2008) 397–404.
- [18] A.Zhu, L.H. Yuan, S.Dai, J.Phys. Chem . C. 112 (2008) 5432–5438.
- [19] S.Naqvi, M. Samim, M.Z.Abdin, F.J. Ahmed, A.N.Maitra, C.K. Prashant, A.K. Dinda. Int.J.Nanomed. 5 (2010) 983–989.
- [20] S.Toyokuni, Free Radic. Biol. Med . 20 (1996) 553–556.
- [21] M.Valko, D. Leibfritz, J.Moncol, M.T. Cronin, M.Mazur, J.Telser. Int. J.Biochem. Cell Biol. 39 (2007) 44–84.
- [22] S.Toyokuni. Redox Rep . 7(2002) 189–197.
- [23] H.Yan, J.C. Zhang, C.X. You, Z.W. Song, B.W. Yu, Y.Shen. Mater . Chem. Phys. 113 (2009) 46–52.
- [24] A.Mukhopadhyay, N. Joshi, K.Chattopadhyay, G.De, ACS Appl. Mater. Interfaces 4 (2012) 142–149.
- [25] R. Rowe, P.J. Sheskey, P.J. Weller. Pharmaceutical Press, 2003.

- [26] M.Hayama, K. Yamamoto, F. Kohori, T. Uesaka, Y. Ueno, H.Sugaya, I.Itagaki, K. Sakai. *Biomaterials* (2003), 25,1019.
- [27] C.R.Cervantes- Sanchez, E. Olaya, M.Testas, N.Garcia – Lopez, G.Coste, G. Arellin, A.Luna, F.E. Krotzsch, J.Surg. Res. (2003), 110, 207.
- [28] (a) Rockenberger J, Scher EC, Alivisatos AP. *J Am Chem Soc* (1999); 121: 11595–6;
(b) Hyeon T, Lee SS, Park J, Chung Y, Na HB. *J Am Chem Soc* (2001); 123: 12798–801;
(c) Sun S, Zeng H, Robinson DB, Raoux S, Rice PM, Wang SX, et al. *J Am Chem Soc* (2004);126:273–9;
(d) Chin SF, Pang SC, Tan CH. *J Mater Environ Sci* (2011); 2: 299–302.
- [29] (a) Vijaya Kumar R, Koltypin Y, Xu XN, Yeshurun Y, Gedanken A, Felner IJ *Appl Physics* (2001);89:6324–8;
(b) Hai TH, Kura H, Takahashi M, Ogawa T. *J Colloid Interface Sci* (2010); 341:194–9;
(c) Phong le V, Hung TQ, Son VT, Kim S, Jeong JH, Kim C, et al. *J Nanosci Nanotechnol* (2011); 11: 2726–9.
- [30] Pinna N, Garnweitner G, Antonietti M, Niederberger M. *J Am Chem Soc* (2005);127: 5608–12.
- [31] Zhou ZH, Wang J, Liu X, Chan HSO. *J Mater Chem* (2001); 11:1704–9.
- [32] Sun J, Zhou S, Hou P, Yang Y, Weng J, Li X, et al. *J Biomed Mater Res A* (2007); BAD:333.
- [33] Wang X, Zhuang J, Peng Q, Li Y. *Nature* (2005); 437: 121–4.
- [34] (a) Wang HW, Lin HC, Yeh YC, Kuo CH. *J Magn Magn Mater* (2007); 310:2425–7;
(b) Yan A, Liu X, Qiu G, Wu H, Yi R, Zhang N, et al. *J Alloys Compd* (2008); 458: 487–91;
(c) Marques RFC, Garcia C, Lecante P, Ribeiro SJL, Noe L, Silva NJO, et al. *J Magn Magn Mater*(2008); 320: 2311–5;
(d) Martinez-Mera I, Espinosa-Pesqueira ME, Perez-Hernandez R, Arenas-Alatorre J. *Mater Lett* (2007);61:4447–51.
(e) Park JY, Patel D, Choi ES, Baek MJ, Chang Y, Kim TJ, et al. *Colloids Surf, A* (2010); 367: 41–6.
- [35] Hui C, Shen C, Yang T, Bao L, Tian J, Ding H, et al. *J Phys Chem C* (2008); 112: 11336–9.
- [36] Wu W, He Q, Jiang C. *Nanoscale Res Lett* (2008); 3:397–415.
- [37] Grabis J, Heidemane G, Rasmane D. *Mater Sci* (2008); 14: 292–5.
- [38] I.Rhee, C.Kim, *J.Magn.Magn.Mater.*261 (2003) 410.
- [39] G.AnandhaBabu, G.Ravi, M.Arivanandan, M.Navaneethan, Y.Hayakawa. *Asian J.Chem.* 25, S39– S41(2013).
- [40] R.Bhatt, I.Bhaumik, S.Ganesamoorthy, A.K.Karnal, M.K.Swami, H.S.Patel, P.K.Gupta. *Physics Status Solidi A*, 209,1,176–180, (2012)
- [41] W.H.Strehlow, E.L.Cook. *J.Phys. Chem.*, 2 (1973) 1.
- [42] S.Tiwari, D.M.Phase, R.J.Choudhary, *Appl.Phys.Lett.* 93 (2008) 234108.
- [43] D.L.A. De Faria, S.V.Silva, M.T.D.Oliveira, *J.Raman Spectrosc.* 28 (1997) 873.
- [44] B.P.Rao, O.Caltun, W.S. Cho, C.Kim, C.G.Kim, *J Magn Magn Mater* 310 (2007) 810–812.
- [45] Shang H, Chang W-S, Kan S, Majetich SA, Lee GU. *Langmuir* (2006); 22: 2516-22.
- [46] Vidal-Vidal J, Rivasb J, Lopez-Quintela MA. *Colloid Surf A* (2006); 288:44-51.
- [47] Veyret R, Delair T, Pichot C, Elaissari A. *J Magn Magn Mater* (2005); 295: 155-63.
- [48] Xu H, Cui L, Tong N, Gu H. *J Am Chem Soc* (2006);128:15582-3.
- [49] Schreiber E, Ziener U, Manzke A, Plettl Al, Ziemann P, Landfester K. *Chem Mater*(2009);21:1750-60.
- [50] Mikhaylova M, Kim DK, Bobrysheva N, Osmolowsky M, Semenov V, Tsakalagos T, et al. *Langmuir* (2004); 20:2472-7.
- [51] D.H.Han, J.P.Wang, H.L.Luo, *J.Magn. Magn. Mater.* 136 (1994) 176 – 182.
- [52] Q.Song, Z.J.Zhang, *J. Am. Chem. Soc.* 126 (2004) 6164-6168.