Synthesis, Characteristics And Magnetic Properties Of Polymer – Ferrite Nanocomposite

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Abstract

The nanocrystalline ferrite of $Cu_{0.2}Ni_{0.8}Fe_2O_4$, synthesized through chemical co-precipitation method and subsequently, coated with intrinsically conducting polymer shell of polypyrrole and polyaniline have been studied. The XRD patterns confirm the formation of nano sized cubic spinel structure in single phase with average crystallite size of ~6 nm. The dc magnetization measurements performed on VSM show the magnetization enhancement in the M-H curves at 20K on polymerization. The value of blocking temperature, TB is found to be increased from 120K to 140 K on polymerization which confirms the increase in crystallite size due to the interaction of polymer chain with nanoparticle surface.

1. Introduction

In contemporary research, the nanocomposite materials have attained fabulous interest in both fundamental points of research and engineering applications. It is significant to modify the surface of nanoparticles so as to hang on to their original physical and chemical properties for long time, leading to the functional composite materials for specified applications. Magnetic polymer nanocomposites can be tailor-made depending on the final applications [1-3]. Polymer coated magnetic nanoparticles are of great technological importance as the coating provides a matrix for binding of the particles and also prevents grain growth and agglomeration. It has well been established that the spinel ferrite particles below a critical size (~20nm), possess single domain super paramagnetic behaviour [4-8] even at room temperature, far above their transition region.

In fact, the surface modification of magnetic nanoparticles brings about quite a lot of prospective to the system surprisingly. Though it finds hard to completely eliminate agglomeration in large

scale commercial synthesis of nanoparticles, coating of nanoparticles with polymers affords the possibility of minimizing it to a great extent. The spinel ferrite nanoparticles, in general, are insulators [9], while exhibiting unique magnetic properties [10]. The coating of these materials with intrinsically conducting polymers (ICPs) like polyaniline (PAni), Polypyrrole (PPy) etc make them as electrical conductors at elevated temperatures, even at room temperature and/or at temperatures close to usually mentioned transition region of the nanoferrites, whilst preserving the original magnetic properties. Thus by combining in a single material, the electrical properties of ICPs and magnetic properties of ferrite nanoparticles, new multifunctional materials have been developed. These materials find several applications in mechanical and electrical devices, magnetic resistive damping, loud speakers, seals, sensors, dampers, refrigeration [11] etc. Magnetic nanoparticles tailored with biocompatible polymers are largely being used in medical diagnosis. For example, magnetic nanoparticles are used in magnetic drug targeting, biological high gradient magnetic selective separation for cell sorting [12, 13], tissue engineering, DNA isolation, magnetic resonance imaging contrast agents and hyperthermia.

In this perspective, the aim of this work is the preparation of nanoferrites using the advanced sol gel auto combustion method and the subsequent synthesis of their nanocomposites with PPy by chemical route. The influences of PPy and the content of magnetic nanoparticles in determining the electrical as well as magnetic behavior of the nanocomposites were studied. The formation mechanism of the self assembled composite nanostructures was also discussed.

2. Experimental

Nanoparticle Synthesis:

The $Cu_{0.2}Ni_{0.8}Fe_2O_4$ nanoparticles have been prepared using a wet chemical process i.e. by the co-precipitation method. A mixed solution of 0.2 M $CuCl_2$ (hydrated), 0.8 M $NiCl_2$ (hydrated) and 2 M $FeCl_3$ (hydrated) was slowly poured in NaOH while keeping pH at 10. The mixture was slowly heated to 85 ^0C. For surface coating the Oleic acid (5 ml) was used. The solution was cooled down slowly while continuous stirring. HNO_3 (Few drops) were added to precipitate the formed coated particles. This precipitate was washed for several times with hot distilled water so as to remove NaCl. Finally, acetone washing was used to remove water. The acetone-wet slurry was dispersed in 20 ml of kerosene and heated at 50 ^0C for 5 min. The resulting fluid was

centrifuged at 12000 rpm for 10 min. The fluid was repeatedly washed with acetone [14] and finally dried. The as prepared sample is hereafter referred to as Pristine.

ICP Coating

A small amount of the nano-particles of $Cu_{0.2}Ni_{0.8}Fe_2O_4$ are first dispersed in de-ionized water using ultra sonication technique. The 200 ml of standardized ammonium peroxodisulphate (APS) was kept to add fractionally to the solution before and after the addition of monomer. The monomer of aniline/pyrrole, keeping monomer: APS mole ratio 1:1.25 was slowly syringed into the dispersion under constant sonication followed by centrifugation at 10000 rpm on complete polymerization. The pH had been maintained just below 7. The residue was then kept overnight in the vacuum oven at about 50 ℃ to get the fine powders of functionally coated surface modified magnetic nano-particles. The two selected composites i.e. $Cu_{0.2}Ni_{0.8}Fe_2O_4$ – PAni (0.5 g/0.025 ml aniline) and $Cu_{0.2}Ni_{0.8}Fe_2O_4$ – PPy (0.5 g/0.025 ml pyrrole) composites hereafter will be referred to as CNPAni and CNPPy respectively

Characterizations

Room temperature XRD patterns of the samples were recorded using a PHILIPS make step scanning mode X'PERT X-ray powder diffractometer (45 keV and 40 mA) with filtered CuKα radiation of wave length 1.5 Å. The 2θ scans were taken from 10 to 90° with a step size of 0.02° and counting time of 10 second per step. Initially the obtained XRD patterns were analyzed and indexed with the help of Powder X program. A silicon disc (cubic a=5.431 A°) has been used as standard sample for internal calibration. The XRD patterns are analyzed and indexed with the help of powder diffraction package (PDP11.1) [15]. This program consists of programs INDEX and REFINE and allows indexing of the powder diffraction pattern and the refinement of the cell parameters using least square method. The dc magnetization measurements of the nanoparticles as well as the nanocomposites were performed using PARC make vibrating sample magnetometer (VSM) model 155.

3. Results And Discussion

Figure 1(a) illustrates the indexed and refined XRD patterns for the pristine $Cu_{0.2}Ni_{0.8}Fe_2O_4$ sample. All the fundamental Bragg reflections in accordance with the JCPDS data are present in the XRD pattern and reflections from impurity phases are absent. These observations clearly

indicating that the sample is formed in single phase and crystallizes in cubic spinel structure with high purity.

The broad diffraction peaks in the X-ray diffractograms indicate that the mean particle size is in the range of nanometer. The XRD pattern for Nanocrystalline $Cu_{0.2}Ni_{0.8}Fe_2O_4$ sample was carried out. The obtained values of the lattice and structural parameters are in good agreement with the values reported in literature for inverse spinel. The estimated average crystallite size in the profile refinement for the Nanocrystalline pristine cubic sample is 4.0 nm.

It is understood from the figure that the cubic spinel structure of nanoparticles of $Cu_{0.2}Ni_{0.8}Fe_2O_4$ retains even after undergo a polymerization treatment in order to encase them with PAni and PPy. However, the parameters like the peak intensities and widths are altered slightly, which may be due to the fact that polymerization has generated some defective/repair states in the system. Also, an Additional broad peak obtained in the XRD patterns of PAni as well as PPy coated nanoparticles of $Cu_{0.2}Ni_{0.8}Fe_2O_4$ at around 25° is attributed to the polymer chain growth effectively over the nanoparticles. The slight decrease in the width of XRD peaks after polymerization suggests that there is an increase in crystallite size.
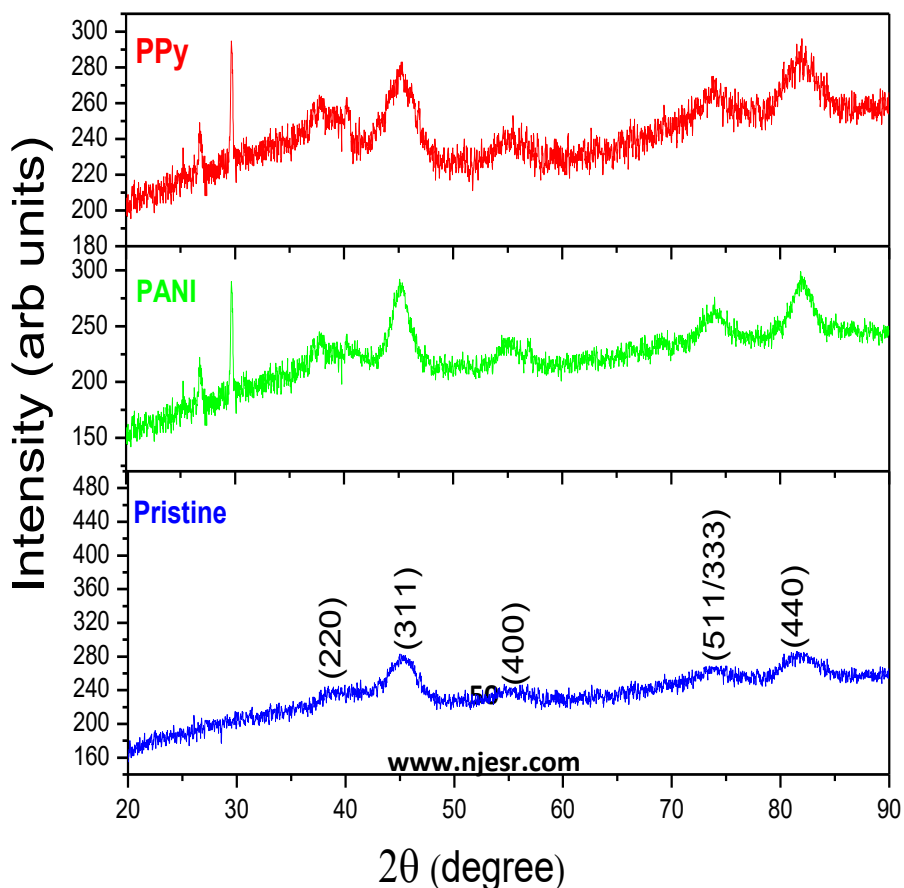
Figure 1: XRD Pattern Obtained For The Pristine, Pani And PPY Coated Samples.

The value of lattice parameters for the pristine, PAni and PPy coated samples of $Cu_{0.2}Ni_{0.8}Fe_2O_4$ are 8.335Å, 8.340Å and 8.343Å respectively. The average particle sizes were estimated with the help of Scherer equation [16] using the width of 311 reflections and found to be about 4.1 nm ,5.2 nm and 5.8nm for Pristine , PAni and PPy coated $Cu_{0.2}Ni_{0.8}Fe_2O_4$ samples, respectively. The x-ray densities of the Pristine , PAni and PPy coated $Cu_{0.2}Ni_{0.8}Fe_2O_4$ samples are calculated to be 5.398 gm/cm^3, 5.388 gm/cm^3 and 5.382 gm/cm^3.

The Bragg reflections are indexed in Fe_3O_4 like cubic closed packing structure and the estimated lattice parameter, *a*, with an accuracy of ±0.002 Å for all the samples reported here, differing slightly from sample to sample, is listed in Table 1.

Figure 2 (a) shows M-H curve recorded at 300 K for the pristine, PAni and PPy coated samples of $Cu_{0.2}Ni_{0.8}Fe_2O_4$. It clearly shows zero remanant magnetization and coercivity, which suggest super-paramagnetic behaviour for all the samples at 300 K. Figure 4.5 shows the hysteresis curves recorded at 20 K for pristine, PAni and PPy coated samples of $Cu_{0.2}Ni_{0.8}Fe_2O_4$. The saturation magnetization (*Ms*) was obtained by extrapolation of *M* vs. *1/H* curve to *1/H* → 0, and it gives the values of 32.6, 42.4and 43.2 emu/g respectively for the three samples which is much less than 98 emu/g, the value for bulk sample of $Cu_{0.2}Ni_{0.8}Fe_2O_4$ [17]. Taking the analogy observed in our earlier work on nanoparticles of $Cu_{0.2}Ni_{0.8}Fe_2O_4$ [18]of 30 Å size by the magnetization measurements, we may attribute the much reduced saturation magnetization in the samples to the frozen disordered spins at the surface [19-20].

As can be seen from the hysteresis curves, the saturation magnetization (Ms) and coercive field (H$_c$) for the PAni and PPy coated samples turned out to be larger than in the sample without polymer material. Such an increase in the magnetization could be attributed to crystallite grain size growth on polymerization [21].

Figure 2(b) shows the hysteresis curves recorded at 20 K for $Cu_{0.2}Ni_{0.8}Fe_2O_4$ samples It could be seen from the figure that the sample lack superparamagnetism at room temperature became ferrimagnetic with finite coercivity and remanance. The much increased value of saturation magnetization could be attributed to crystallite size growth on heating along with surface spin
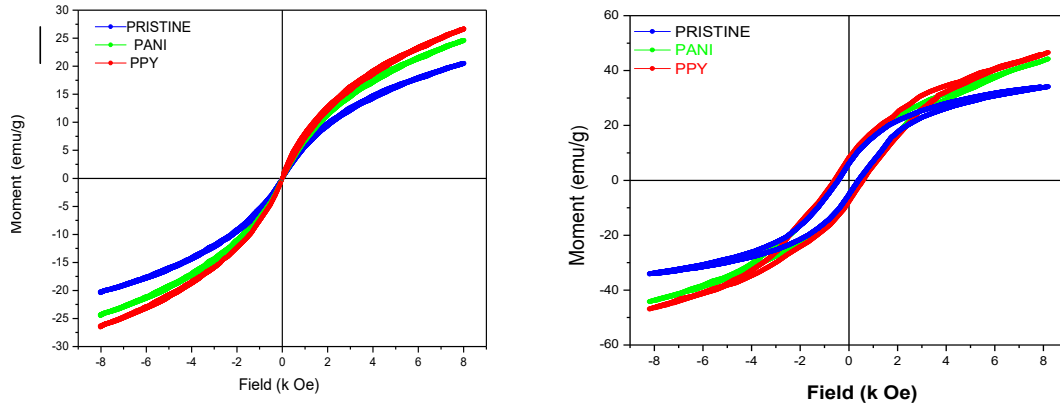
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Figure2: M – H curves for Pristine, Pani, and PPY coated samples at (a) 300k and (b) 20k.

Table1. Structural, Magnetic And Dielectric Parameters Of Pristine, Pani and PPy Coated nanocrystalline $Cu_{0.2}Ni_{0.8}Fe_2O_4$.

Parameters	Pristine	PAni	PPy
Average particle Size (t)	4.1 nm	5.2nm	5.8nm
Lattice Parameter (a)	8.335 Å	8.340 Å	8.343 Å
x-ray density (ρ_x)	5.398 gm /cm^3	5.388gm /cm^3	5.382 gm /cm^3
Saturation magnetization (M_s)	32.6 emu/g	42.4 emu/g	43.2 emu/g
Coercivity (H_c)	1.5kOe	3.2 kOe	3.8kOe
Blocking temperature (T_B)	120k	132k	140k

Figure 3 shows M-T curves recorded in field cooled (FC) and zero field cooled mode (ZFC) for the three samples at 400 Oe field. The divergence of FC and ZFC curve along with an appearance of peaks in the ZFC curves, for the three samples is assigned to the blocking mechanism owing to the competition between thermal energy and magnetic anisotropy energy of nanoparticles. The much broader peaks in the ZFC curves for polymer coated samples compared to the pristine $Cu_{0.2}Ni_{0.8}Fe_2O_4$ samples suggesting larger distribution of grains in the polymerized samples which in turn might be due to the non-uniform coating mechanism. Also, the *M-T* curves for the three samples in ZFC mode show super paramagnetic behaviour above their

blocking temperature T_B. The value of T_B increases from 120K to 132K (Pani Coated), 140 K (PPy coated) on polymerization which again confirms the increase in Crystallite size on polymerization.
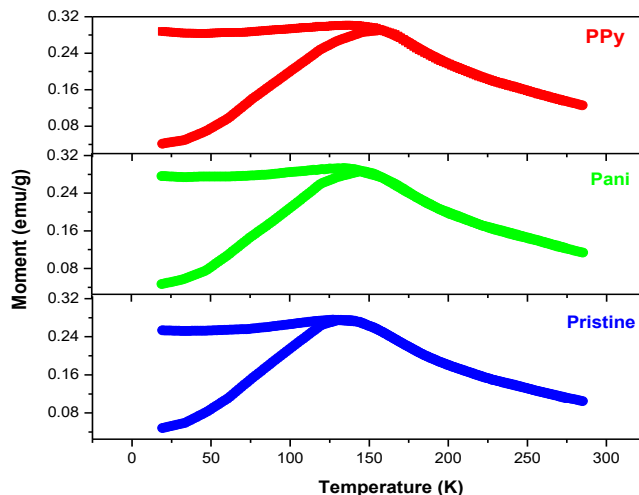

Figure 3: M – T Plots of Pristine, Pani and PPY coated Samples in ZFC and FC modes.

4. Conclusion

The nanocrystalline $Cu_{0.2}Ni_{0.8}Fe_2O_4$ could be synthesized via wet chemical process and surface functionalized with PAni and PPy respectively. From the XRD line broadening yields an average particle size of 4.1 nm. The surface functionalization of the nanoparticles of CaFe2O4 was made possible effectively by the chemical synthesis of polyaniline and polypyrrole shells over the nanoparticles. From XRD, the formation of PAni and PPy shells over the nanoparticles of CaFe2O4 could be confirmed. The obtained magnetization studies revealed that on polymerization, additional magnetic properties are tailored over the nanoparticles; an increase in TB, saturation magnetization and remanent magnetization were observed. This enhancement in magnetization and TB confirms the growth of crystallites on polymer coating which was estimated by XRD.

References

1. S. Taylor, L. Ou, Biomacromolecules, 5 (1) **(2004)** 245-248.
2. K. Hasirsci, J. D. Lewandrowski, "Versatility of biodegradable biopolymers: degradability and an in vivo application" Journal of Biotechnology, 86 **(2001)** 135-150.

3. A. Vila. A. Sanchez, M. Tobio, P. Calvo and M. J. Alonso "Design of biodegradable particles for protein delivery" Journal of controlled Release, 78 **(2002)**15-24.
4. B. Martinez, A. Roig, X. Obradors, E.Molins, A. Rouanet, C. Monty, "magnetic-properties of γ- Fe2O3 nanoparticles obtained by vaporization condensation in a solar furnace", J. Appl. Phys., 79 (5) **(1996)** 2580-2586.
5. S. Yatsuya, T. Hayashi, H. Akoh, E. Nakamura, T. Akira, "Magnetic Properties of Extremely Fine Particles of Iron Prepared by Vacuum Evaporation on Running Oil Substrate" Jpn. J. Appl. Phys. 17**(1978)** 355.
6. R. B. Goldfarb, C. E. Patton, "Superparamagnetism and spin-glass freezing in nickel-manganese alloys "Phys. Rev. B 24 **(1981)** 1360.
7. S. K. Khanna, S. Linderoth, "Magnetic behavior of clusters of ferromagnetic transition metals," Phy. Rev. Lett. 67 **(1991)** 742.
8. J. P Chen, C. M Soresen, K. J Klabunde, G. C Hadjipanayis . "Size-dependent magnetic properties of MnFe2O4 fine particles synthesized by co precipitation" J. Appl. Phys. 76 **(1994)** 6316.
9. Coey J.M. D, Berkowitz A E, Balcells.L.I. Putris F F and A Barry, "Magnetoresistance of Chromium Dioxide Powder Compacts" Appl. Phys. Lett. 80 **(1998)** 3815.
10. V. A. M Brabers, In: Hand Book of Magnetic Materials, ed. By K. H. Buschow (Elsevier Science B. V.) 8 **(1995)** 189.
11. M. R. Zacharia, M.I Aquino, R.D. Shull, E.B. Steel, "Formation of Superparamagnetic nanocomposites from vapor phase condensation in a flame", Nanostruct. Materials, 5. **(1995)** 383-392.
12. J. K Ruuge, A.N. Ruzetski, magnetic fluids as drug carriers: Targeted transport of drugs by a magnetic field, J. Magn. Mater. 122 (1-3) **(1993)** 335-339.
13. N. M Pope, R.C. Alsop, Y.A. Chang, A.K smith, Evaluation of magnetic alginate beads as a solid support for positive selection of CD34+ cells, J. Biomed. Mat. Res. 2 **(1994)** 449-457.
14. S. N. Dolia, R. Sharma, M. P. Sharma, N. S. Saxena and S. K. Jain, Ind. J. Pure Appl. Phys. **(2006)** 44 774.
15. M. Calligaris and S. Geremia, Powder diffraction package version 11.1, Dipartmento di science chemiche, universita di Trieste **(1990)**.
16. B.D. Cullity, (ed.): Elements of X-ray Diffraction, p. 132. Wesley, Reading **(1959)**.
17. S. Manjura Hoque, M. Amanullah Choudhury and F. Islam, J. Magn. Magn. Mater. 251 **(2002)** 292.
18. R. H. Kodama and A. E. Beronitz, Phys. Rev. B **(1999)** 29 6321.
19. S.N. Dolia, R. Kumar, S. K. Sharma, M.P. Sharma, S. Chander, M. Singh, Current Appl. Phys. **(2008)** 8 620.
20. J.M.D. Coey: Phys. Rev. Lett. Vol. 27 **(1971)** 1140.