

Magnetic Behaviour of $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ and Polyaniline Nanocomposites Synthesised by Reverse Microemulsion

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Abstract—*Polyaniline (PANI) is known to be a widely studied conducting polymer and spinel ferrites constitute a class of magnetic materials with immense application possibilities and tunable magnetic properties. In the present study we demonstrate reverse microemulsion yielding cobalt zinc ferrite/ PANI nanocomposites with controlled morphology using soft template method. FTIR, XRD, SEM and TEM measurements have been carried out in order to obtain the detailed structural characterization. The micrographs revealed the formation of spherical cobalt zinc ferrite nanoparticles supported on PANI nanofibre.*

The magnetic properties of the nanocomposites were investigated with the help of Vibrating Sample Magnetometer (VSM); a transition from superparamagnetism to ferromagnetism was found to accompany the nanocomposite formation.

1. INTRODUCTION

With the advancement in nanoscience and nanotechnology research efforts are being made on synthesizing new types of bifunctional nanocomposites with controllable shapes, sizes and assemblages, with novel and tunable properties useful for a wide range of applications. Combining an organic polymer with inorganic material would result in a synergic behaviour that is difficult to obtain from individual components. This has lead to broad technological applications of these nanocomposites [1,2].

The present study describes synthesis of $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ /PANI nanocomposites via reverse microemulsion technique [3,4]. PANI (polyaniline) is the most extensively studied conductive polymer due to its relatively facile processability and excellent environmental stability combined with relatively high levels of electronic conductivity as well as thermoelectrical and optical properties [5, 6].

Magnetic nanoparticles are known to exhibit unique properties such as enhanced magnetic moments, exchange-couple dynamics, quantization of spin waves and giant magneto resistance leading to new potential applications in permanent magnets, data storage devices and targeted drug delivery [7, 8].

Thus, the present study was carried out with the objective to investigate the alignment of $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ ferrite nanocrystals on PANI nanofibres and to study the effect of PANI on magnetic properties of the nanocomposites formed. The structural characterizations were carried out by FTIR, TEM, and XRD and magnetic properties were studied using Vibrating Sample Magnetometer (VSM).

2. EXPERIMENTAL SECTION

Synthesis of $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ ferrite nanocrystals by reverse microemulsions process was done by preparing two reverse microemulsions ME_1 and ME_2 . In ME_1 , the aqueous phase was composed of stoichiometric amounts of 0.5M FeCl_3 , 0.12M $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 0.125M ZnCl_2 and in ME_2 , the aqueous phase was made of 0.5M NaOH solution.

The microemulsion ME_2 was slowly added to ME_1 with constant heating at a temperature of 80°C. Appearance of blackish-brown colour of ferrite crystals mark the completion of reaction. The reaction mixture was further stirred for 4 hours on magnetic stirrer, centrifuged at a speed of 10,000rpm for 20min followed by repeated washing by methanol and double distilled water and finally drying in vacuum oven at 100°C for 48 hours. The pH of the reaction was maintained at 12.

In addition to this, two quaternary microemulsions, ME_3 and ME_4 were also prepared. ME_3 contained cyclohexane as the oil phase with CTAB and isoamyl alcohol as the surfactant and co-surfactant respectively. The aqueous phase was made of aniline and the dopant solution. 0.005g of magnetic $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles were dispersed in it. ME_4 was similar to ME_3 , except for the difference in the aqueous phase that contained the initiator, ammonium per sulphate in place of aniline.

Microemulsions ME_4 was added drop wise to ME_3 under constant stirring at room temperature and the mixture was further stirred for 24 hours under inert atmosphere.

Protonated emeraldine formation was confirmed by the appearance of green colour, which was centrifuged at 5000rpm, followed by repeated washing with methanol and double distilled water, before finally drying in a vacuum oven at 50°C for 48 hours.

3. RESULTS AND DISCUSSION:

X-ray diffraction pattern of $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ ferrite nanocrystals, the PANI nanostructure and $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{PANI}$ nanocomposites are given in the Fig. 1[(a) - (c)].

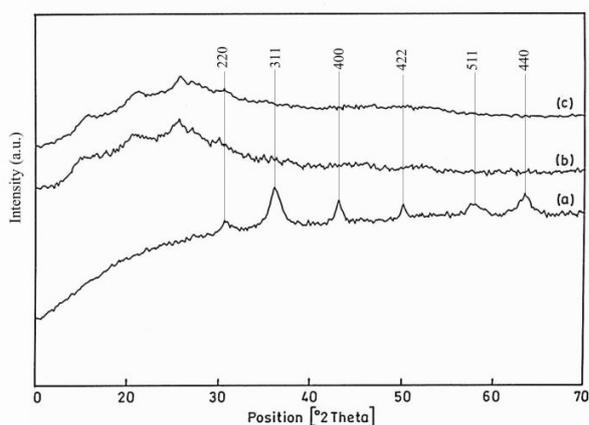


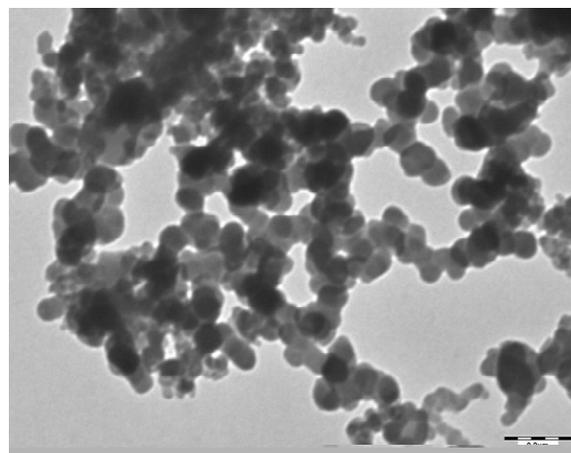
Fig. 1: XRD patterns of (a) $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ ferrite nanocrystals, (b) PANI nanofibres and (c) $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{PANI}$ nanocomposites obtained from reverse microemulsion.

Fig. 1(c) reveals a diffused broad amorphous halo over the 2θ range of 10-30° and broad reflections around 15°, 21° corresponding to large molecular weight PANI. The presence of diffused broad peaks indicates lower crystalline order owing to the formation of larger fraction of PANI [8]. On comparing the XRD pattern of pure ferrites with that of the nanocomposites formed, it becomes evident that the crystalline nature of ferrites gets suppressed on the formation of nanocomposites.

Broad reflection around 2θ value of 26° indicates planar configuration of phenyl rings in PANI. This configuration facilitates extensive interchain π - π orbital overlap and thus leads to greater stabilization via resonance [9]. The presence of this peak in both the spectra – i.e. pure PANI and in the composite indicates fibrous structure, which gets confirmed by the TEM. The TEM micrographs of $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanocrystals, PANI fibres and $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{PANI}$ are presented in Fig. 2 [(a)-(c)].

Monodispersed spherical nanoparticles of $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ having an average diameter of 6 nm are obtained using microemulsion technique. PANI fibres having an average diameter of 20 nm are obtained using CTAB/ iso-amyl system. PANI/ $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanofibres are found to possess

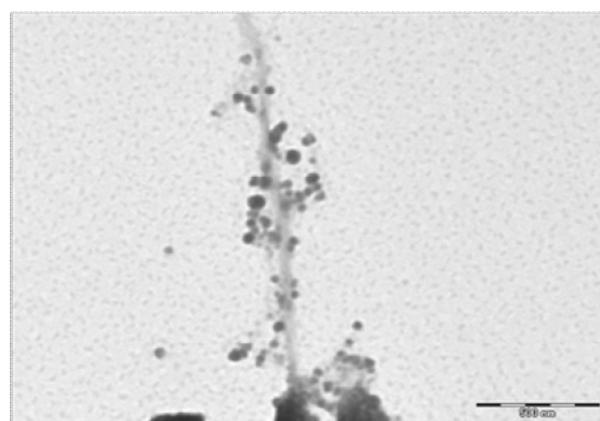
bimodal distribution, where $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles align upon PANI nanofibres. The TEM micrographs presented here were taken after centrifugation and complete drying of the product formed.



(a)



(b)



(c)

Fig. 2: TEM micrographs of (a) $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ ferrite nanocrystals, (b) PANI nanofibres and (c) $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{PANI}$ nanocomposites obtained from reverse microemulsion.

3.1 Magnetic Properties

The room temperature magnetization versus applied field curve of pure nanocrystalline ferrite shows its superparamagnetic character whereas that of PANI/ferrite nanocomposites as depicted in Fig. 3, shows ferromagnetic behaviour. In ferrite nanoparticles, magnetization is still far from saturation; with a lower magnetization value M_S of 11.74 emu/g at 300K. Typical 'S'-like shape of the curve, absence of hysteresis, negligible remanence and coercivity indicate a superparamagnetic character and single domain in the nanocrystalline $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ ferrite [10].

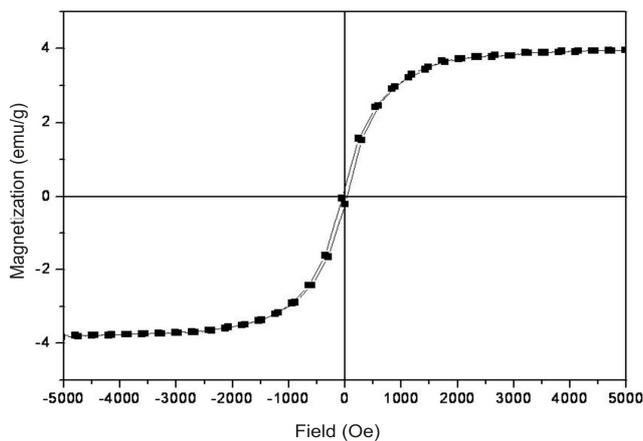


Fig. 3: The hysteresis loops of $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{PANI}$ nanocomposite obtained from reverse microemulsion measured at 300 K.

The magnetization versus applied field curve of the nanocomposites at room temperature shows a hysteresis loop and saturation magnetization at 3.95 emu/g at 300K with the available maximum field indicating their ferromagnetic behaviour.

The magnetic properties of nanoparticles are a combination of many anisotropy mechanisms such as magnetocrystalline anisotropy, surface anisotropy and interparticle interactions. The alignment of $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ ferrite nanoparticles with PANI nanofibre is likely to effect the contribution towards the surface anisotropy K , which is related to the energy barrier (E_A) of rotation of magnetization orientation in single domain particles by Stoner-Wohlfarth theory and is given by:

$$E_A = KV \sin^2\theta$$

Where θ is the angle between the applied magnetic field and the easy axis of the nanoparticles [11]

The interaction between PANI nanofibres and $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ ferrite may be attributed to H-bonding between -O- of the ferrite and hydrogen of -N- of PANI nanofibre. Nanofibres have perfect geometrical orientation for strong H-bond. This leads to an increase in the anisotropy, as a result the activation energy barrier also increases following the above equation and thus higher applied field is required for spin reversal.

Secondly, ferrite nanoparticles are aligned linearly on PANI nanofibre, which makes them stay in close proximity to each other therefore increases the exchange interaction (interparticle interaction). This, also in turn results in increase of coercivity. There have been reports of increase in coercivity for ferrofluid samples when interparticle interactions are high [12].

4. CONCLUSION

Here, we endeavour a facile synthetic route for obtaining bimodal (bifunctional) $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{PANI}$ nanocomposites. This work would result in a synthetic strategy for obtaining morphologically controlled nanocomposites. Highly superparamagnetic $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles transform to ferromagnetic materials on formation of nanocomposite with PANI.

The present method has the potential to be extended for the fabrication of many more nanocomposites with bimodal size distribution having applications in catalysis support, biomedicine applications and in magnetic shielding.

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REFERENCES

- [1] Zhang, Z.; Wan, M. *Synth. Met.* 2003, 132, 205.
- [2] Gomez-Romero, P. *Adv. Mater.* 2001,13, 163
- [3] Zhang-ai, H; Hong-Xiao, Z; Chao, K.; Yu-ying, Y.; Xiu-li, S.; Li-jun R, Yan-peng, W. *J. Mater. Sci. Electr.* 2006,17,859.
- [4] Wu, K. H.; Shin, Y. M.; Yan, C. C.; Ho, W. D.; Hsu, J.S. *J. Polym Sci Part A: Poly Chem.* 2006,44, 2657.
- [5] Huang, W. S.; Humphrey, B. D.; MacDiarmid, A. G. *J. Chem. Soc., Faraday Trans.* 1986, 82, 2385.
- [6] Majidi, M.R.; Kane-Maguire, L. A. P. ; Wallace, G. G. *Polymer* 1994, 35, 14, 3113
- [7] Alivisatos, A.P. "Semiconductor Clusters, Nanocrystals, and Quantum Dots," *Science* 1996, 271, 5251, 933.
- [8] Yavuz, Ö.; Ram, M.K.; Aldissi, M.; Poddar, P.; Hariharan, S. *J. Mater Chem.* 2005, 15, 810.
- [9] Luzny, W.; Sniechowski, M.; Laska, J. *Synthetic Metals*, 2002, 126, 27.
- [10] Kumar, S.; Singh, V. et.al., *Inorganica Chimica Acta*, 2015, 428, 21-26.
- [11] Stoner, E.C.; Wohlfarth, E. P. *Phil. Trans. Roy. Soc. (London)* 1948, A240, 599.
- [12] El-Hilo, M.; O'Grady, K.; Chantrell ,R.W. *J. Magn. Magn. Mater.* 1992, 114, 295.