

Enhanced Magnetic Properties of Polymer-Magnetic Nanostructures Synthesized by Ultrasonication

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Abstract

Polymer based nickel (Ni) and cobalt (Co) co-doped ferrites were prepared by adept ultrasonication route. Different concentrations of polymer [polyvinyl alcohol (PVA)] (0.2 g and 0.5 g) was added as a surfactant to the magnetic particles. The phase purity of Ni-Co ferrites (spinel structure) was confirmed by X-ray diffraction (XRD). Enhanced saturation magnetization of polymer based magnetic nanoparticles due to shape anisotropy and size. 0.2 wt% doped ferrite showed superparamagnetic characteristics with blocking temperature above room temperature. Hence, ultrasonication route is a rapid and effective technique for tailoring size and morphology of magnetic nanostructure that could be useful in magnetic-sensor applications.

Keywords: Ultrasonication; Magnetic Nanostructures; Polymers; Nanocomposites; Magnetization.

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1. Introduction

Nanosized particles possess distinct chemical and physical properties owing to their surface-to-volume ratio [1]. Generally, nanocomposites contain nanometric metals or metal oxide particles embedded in polymer matrices that provide a diverse range of magnetic and electrical properties. Cobalt ferrite (CoFe_2O_4) is a familiar hard magnetic material which has been widely studied due to its exciting magnetic properties [2]. However, nickel ferrite (NiFe_2O_4) is a soft ferrite which possesses low magneto-crystalline anisotropy but high electrical resistivity, and is used for power applications [3]. Inorganic ferrite materials were embedded in organic matrix for wide range of applications in electromagnetic interference (EMI), shielding [4-5], drug delivery [6] and magnetic resonance imaging (MRI) [7-10]. Various techniques have been suggested to synthesize nanophase materials such as mechanical milling [11], reversed micelles [12] and self-assembled monolayer [13]. Apart from above mentioned techniques, ultrasonication is a homogenizer to diminish particles size in a liquid to improve uniformity and stability. It is an efficient method to reduce the size of soft and hard magnetic particles. Dispersion and deagglomeration of particles in liquids are the significant application of ultrasonicator. Ultrasound can be employed to aid extraction, homogenization, freezing, crystallization, filtration and drying process [14]. Ultrasonication method has been employed in the prepared of uniform sized nanostructures of metals, metal oxides, graphene, and polymer nanocomposites for several applications.

Particle size, distribution of particles and morphology may not be controlled during conventional synthesis process. This could be solved by employing polymers, surfactants or capping agents. However, it is indistinguishable to comprehend the mechanism of variation in particle size, distribution and morphology of the particles. Polymers were coated on the surface of nanoparticles for protecting oxidation and to provide well controlled growth to tailor morphology of the nanoparticles. Nathani et al. reported the magnetic behavior of mechanical milling of nickel ferrite and polyethylene by in-situ polymerization of nickel ferrite polystyrene nanocomposites with core-shell morphology of particles [15]. Xiang et al. reported on polyvinyl pyrrolidone based cobalt–nickel ferrite nanofibers by electrospinning route. They found that the saturation magnetization and coercivity lie in the range 29.3–56.4 emu. g^{-1} and 210–1255 Oe, respectively [16]. Zhang et al reported decrease in coercivity and increase in magnetization of NiFe_2O_4 magnetic nanorods via a Poly (ethylene glycol) PEG-assisted route [17]. Polyvinyl alcohol (PVA) is semi-crystalline, non-toxic, biocompatible,

biodegradable polymer with good chemical resistance which is employed for biomedical applications [18]. In literature, very few studies related to magnetic polymer nanocomposites via ultrasonication assisted technique are reported. Chitra et al. reported ultrasonication on polyaniline/NiCoFe₂O₄ which showed spherical morphology with increase in magnetic saturation [19]. However, to the best of our knowledge, no reports available on polyvinyl alcohol (PVA) based hard soft ferrites synthesized by ultrasonication route to examine physicochemical and magnetic properties.

2. Materials and Methods

Polymer based nickel-cobalt co-doped ferrites (NiCoFe₂O₄) was prepared by ultrasonication route using precursors such as ferric chloride (Merck), nickel (II) chloride hexahydrate (Merck), cobalt chloride hexahydrate and poly-vinyl alcohol (PVA) (CDH laboratory reagents). Solutions of FeCl₃ (0.4 M), NiCl₂.6H₂O (0.1 M) and CoCl₂.6H₂O (0.1 M) were mixed at 60 °C for 30 min. Subsequently, hydrazine hydrate is added drop wise to the solution which transformed into black colored solution. Final solution was ultrasonicated using Sonics-Vibra-Cell VCX (750W) 750 probe ultrasonicator with pulse time (three min) for 30 min. Ultimately, the solution was dried in hot air oven at 80 °C and grounded to obtain fine powders. Hereafter, it is referred as UNCF. The polymer (PVA) with different concentrations (0.2 gm and 0.5 gm) was added separately to Ni-Co ferrites solution to synthesize polymer based magnetic nanostructure and the samples are labeled as 0.2PUNCF and 0.5PUNCF, respectively.

3. Results and Discussion

3.1. XRD analysis

X-ray diffraction (XRD) of the samples was carried out using Bruker XRD CuK_α radiation (0.154 nm). Fourier transform infrared spectroscopy (FTIR) and Raman analysis of the samples were examined using BOMEMDA-8 FTIR and Jobin Yvon, respectively. The surface morphology was analyzed by scanning electron microscopy (SEM) (Carl Zeiss MA15/EVO18). Magnetic properties of the magnetic nanostructures were carried out by vibrating sample magnetometer (VSM) in a physical property measurement system (PPMS) from Quantum design.

The XRD patterns of (a) UNCF, (b) 0.2PUNCF and (c) 0.5PUNCF are shown in Fig. 1A. The major peaks are associated with (220), (311), (400), (422), (511) and (440) planes of NiCoFe₂O₄ using JCPDS (03-0864) and JCPDS (10-0325) values. The average crystallite size and lattice parameter were calculated using MAUD (Material Analysis Using Diffraction) software and the values are shown in Table 1. The crystallite size was around 105 nm for UNCF sample. The decrease in crystallite size was observed for 0.2PUNCF which could be due to high temperatures and pressures at microscopic level of the sonicated composite in colloidal solution by the formation of acoustic cavitation [20]. As the polymer incorporation increases to 0.5 wt% of PVA to UNCF, the crystallite size was enhanced which might be due to the increase in chemical activity of polymer chains. The chemical activity is increased by the acoustic cavitation by creating radical reactions in the solutions [19]. The lattice parameter decreased upon incorporation of polymer into Ni-Co ferrites. Wang et al. reported increased lattice parameter (8.366 Å) for CoFe₂O₄ and 8.342 Å for NiFe₂O₄ [3]. For 0.5PUNCF, the (220) plane is a prominent compared to other planes which could be due to growth kinetics plane directions. The intense (311) plane was attained for 0.2PUNCF. Ultrasonication and polymer incorporation change the growth rate which could modify the plane orientation as observed in 0.2PUNCF and 0.5PUNCF samples.

3.2. FTIR

FT-IR spectra of UNCF and 0.5PUNCF are shown in the Fig. 1B. A broad absorption band was observed between 3841 cm⁻¹ and 3200 cm⁻¹ which corresponds to O-H stretching band of complex metal-hydroxyl groups. The bands at 3435 cm⁻¹ and 1609 cm⁻¹ could be due to OH stretching vibration through hydrogen bonding in metal oxides. Adsorbed atmospheric CO₂ in trace level was confirmed by absorption peak at around 2367 cm⁻¹ which assigned to C=O stretching vibrations of carboxylate group of CO₂ gas. The peak at 1403 cm⁻¹ was attributed may be also due to adsorption of carbonate group [21]. The peak at 1200 cm⁻¹ is attributed to C-OH stretching vibrations [22]. The peak at 1380 cm⁻¹ is assigned to symmetric stretching of CO₃²⁻ [23]. The peak at about 1560 is attributed to the NH₂ group may be due to hydrazine [24]. The Fe–O bond in tetrahedral and octahedral sites in NiCoFe₂O₄ was observed at 638 cm⁻¹.

Table 1 Average crystallite size and lattice parameter of polymer based nickel and cobalt ions co-doped ferrites

Sample code	Crystallite size (nm)	Lattice parameter
		a=b=c (Å)
UNCF	105	8.200
0.2PUNCF	60	8.000
0.5PUNCF	98	7.800

The metal oxygen band at 590 cm^{-1} was observed which corresponds to intrinsic stretching vibration of metal at tetrahedral site. Cobalt ion substitution in spinel ferrites was observed at the peak 1087 cm^{-1} . The band of stretching mode of the metals was found to be in the range of $600\text{--}500\text{ cm}^{-1}$ [12]. The bands in the range $600\text{--}500\text{ cm}^{-1}$ and 1087 cm^{-1} were suppressed upon addition of PVA into $\text{NiCoFe}_2\text{O}_4$ which confirmed the functionalization of Ni-Co ferrites with PVA by forming hydrogen bond [13].

3.3. Raman Analysis

Raman spectra of (a) UNCF, (b) 0.2PUNCF and (c) 0.5PUNCF are shown in Fig.1C. Five Raman active modes ($A_{1g} + E_g + 3F_{2g}$) are observed in Ni-Co ferrites. The less intense peak at 680 cm^{-1} corresponds to symmetric stretching of oxygen atoms with Fe-O (and Ni-O) bonds in the tetrahedral sites. E_g mode was observed at 320 cm^{-1} which corresponds to symmetric bending mode of oxygen bonding to metal ions. The peaks at 480 cm^{-1} and 530 cm^{-1} are ascribed to asymmetric bending mode of oxygen [$F_{2g}(3)$] and asymmetric stretching mode of iron (nickel, cobalt) and oxygen [$F_{2g}(2)$] modes, respectively. Translational movement of tetrahedron [$F_{2g}(1)$] was observed at 210 cm^{-1} [14,19]. Addition of polymer to Ni-Co ferrites, suppressed all four Raman modes and except the mode $F_{2g}(3)$ which confirmed surface functionalization of the polymer to metal oxides by forming hydrogen bonding. Raman modes of the polymer were observed at 1362 cm^{-1} and 1604 cm^{-1} which corresponding to C-H bending mode of polymer and the first-order scattering (E_{2g} mode), respectively [25].

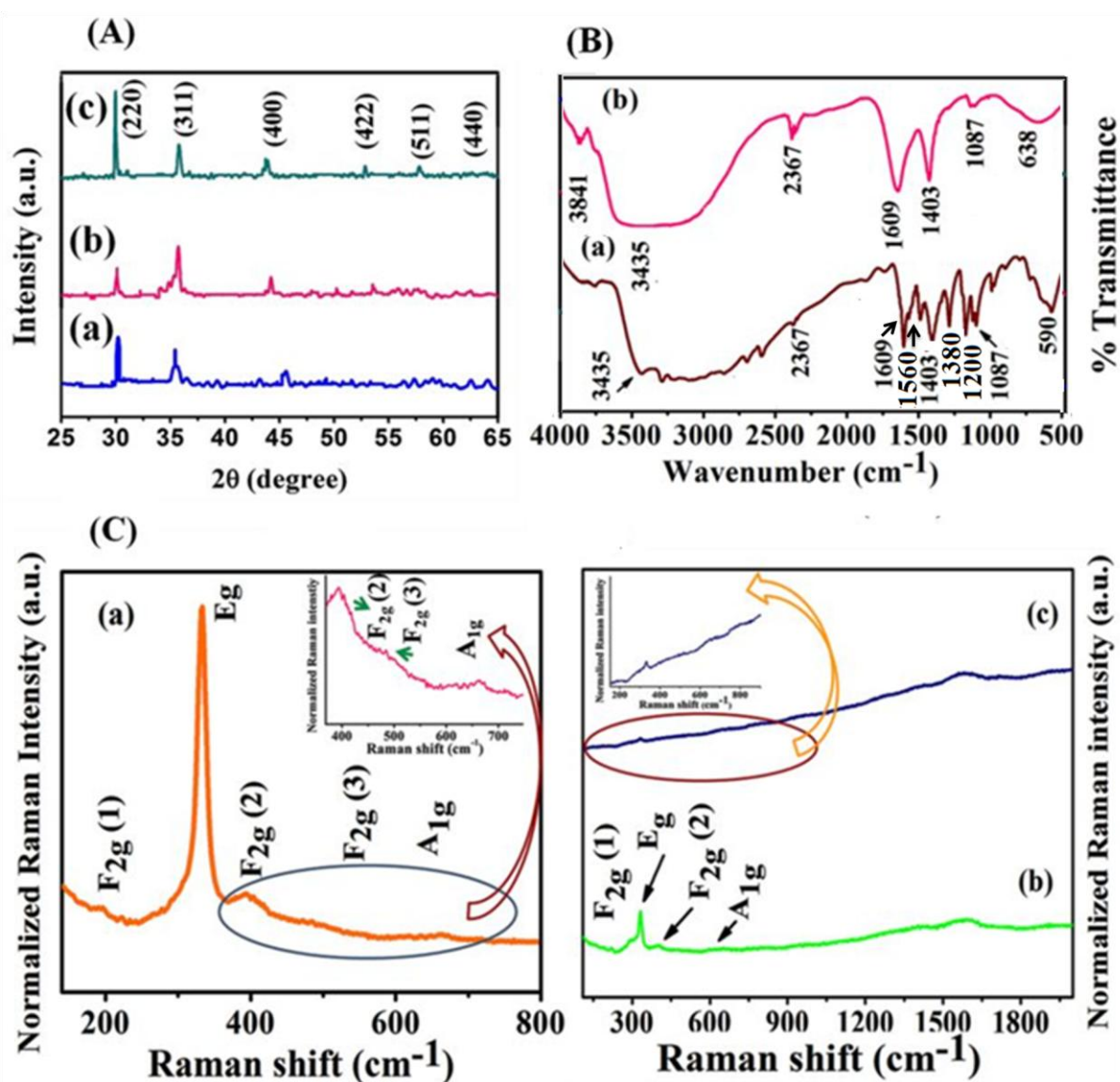


Fig. 1A. XRD patterns of (a) UNCF, (b) 0.2PUNCF and (c) 0.5PUNCF; **Fig.1B.** FTIR spectra of (a) UNCF and (b) 0.5PUNCF; **Fig. 1C.** Raman spectra of (a) UPNCF, (b) 0.2PUNCF and (c) 0.5PUNCF (inset of Fig. 3(c) is magnified portion of spectra from 200 cm^{-1} to 900 cm^{-1}).

3.4. SEM Analysis

The SEM images of $\text{NiCoFe}_2\text{O}_4$ without and with polymer incorporation are shown in Fig. 2. Spherical nanoparticles of $\text{NiCoFe}_2\text{O}_4$ were in the range of 500 nm to 700 nm in the absence of polymer (PVA). Wang et al. reported the synthesis of cubical spinel $\text{M}^{\text{II}}\text{Fe}_2\text{O}_4$ ($\text{M} = \text{Co}, \text{Mn}, \text{Ni}$) with high crystalline structure at 10 min irradiation by microwave [26]. Addition of PVA into Ni-Co-ferrites and ultrasonication leads to modification of the morphology to self-assembled bead like patterns (Fig.2b). The size of beads was in the range 400-600 nm. The

formation of self-assembled bead could be due to the polymer and radical reaction in the solution by acoustic cavitation. At higher concentration (0.5 wt%) of PVA, rectangle ($\sim 100 \text{ nm} \times 300 \text{ nm}$) shaped morphology was observed which is due to the enhanced growth kinetics and chemical activity by acoustics (Fig.2c) [26-28]. CoFe_2O_4 nanocrystals can be prepared with a controlled shape of nearly spherical or cubic shape of the CoFe_2O_4 . Shape is a dominating factor for the coercivity of nanocrystals because, of surface anisotropy [29]. PEG (Polyethylene glycol) with an ordered chain structure is adsorbed at the surface of metal oxide colloid and decreased its activities by the polymer [30]. The addition of PEG to the metal oxide colloids will change the kinetics of the growing colloids, which leads to anisotropic growth of the nanocrystals [31]. In the present case, while adding PVA to $\text{NiCoFe}_2\text{O}_4$, the morphology was modulated due to variation in growth kinetics of metal oxide, not only because of polymer but also by acoustic cavitations.

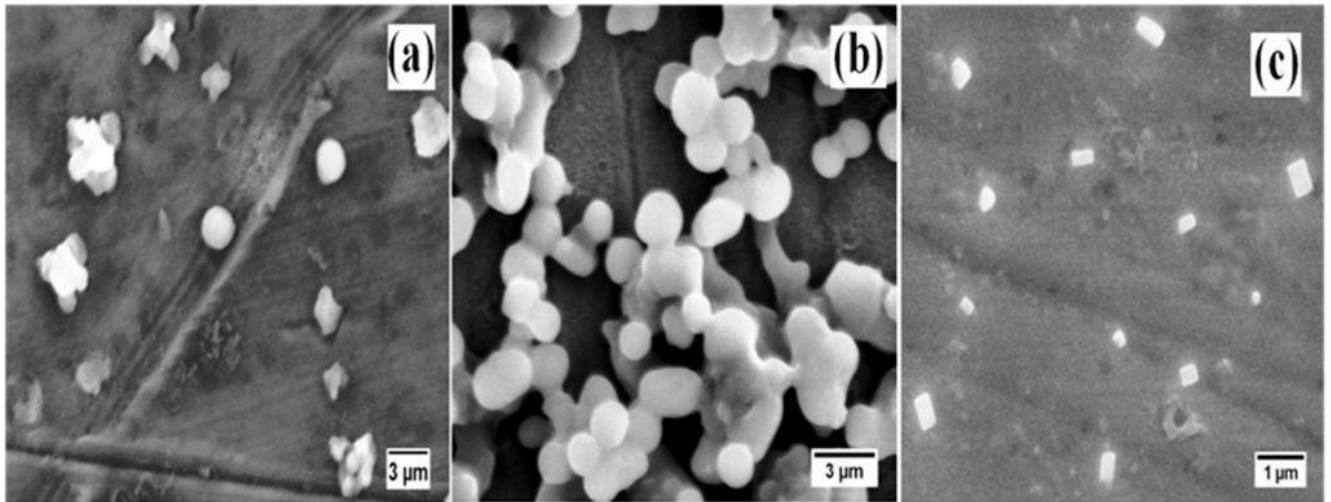


Fig. 2. SEM images of (a) UNCF, (b) 0.2PUNCF and (c) 0.5PUNCF

3.5. Magnetic measurements

Magnetic properties of UNCF, 0.2PUNCF and 0.5PUNCF were studied using vibrating sample magnetometer. Field dependent magnetization curves for UNCF, 0.2PUNCF and 0.5PUNCF at 300 K are shown in Fig.3. The UNCF and 0.5PUNCF showed paramagnetic behavior where magnetization increased with increasing the magnetic field. The 0.2PUNCF sample exhibited contribution from a ferromagnetic phase on top of paramagnetic signal. The saturation magnetization (M_s) of 0.2PUNCF was much higher than the 0.5PUNCF and UNCF samples. Enhanced saturation magnetization (M_s) of 0.2PUNCF compared to 0.5PUNCF and UNCF could be due to oxygen vacancies, spin exchange interaction and shape anisotropy [32]. Inset to the Fig. 3 illustrates the coercive magnetic field and remanent

magnetization (M_r). The coercivity and M_r for UNCF sample was 880 Oe and 0.02 emu/g respectively. For 0.2PUNCF coercivity and M_r for UNCF sample was 130 Oe and 0.01 emu/g correspondingly. The 0.5PUNCF showed similar M_r as to 0.2PUNCF but had a higher coercivity of 305 Oe. Decrease in coercivity by adding polymer to Ni-Co ferrites can be explained by domain structure, strains, crystalline anisotropy and shape anisotropy [33-34].

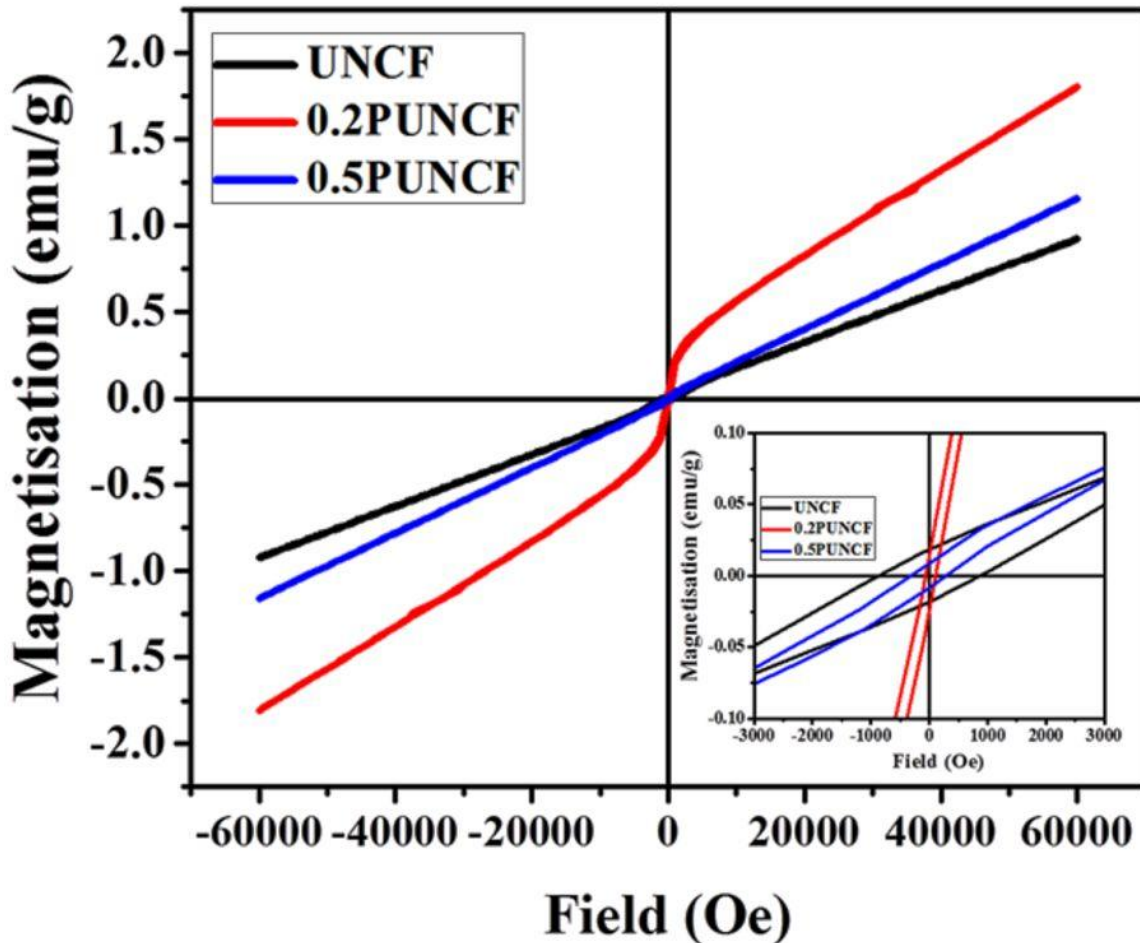


Fig.3. M (H) curves of (a) UNCF, (b) 0.2PUNCF and (c) 0.5PUNCF at 300 K (inset figure is magnified portion of M(H) from -3000 O_e to 3000 O_e).

The presence of shape anisotropy can considerably enhance the magnetic properties of nanoparticles [35]. Shape, crystallinity and magnetization direction play significant role in determining the magnetic properties of the magnetic materials. At the surface of the grains, the modulation in cations coordination and breaking of bond may cause exchange fields as well as canting of spin or disorder in crystal field which activate surface anisotropy [36]. Wu et al. reported that the saturation magnetization reduces as cube sizes decreased due to increase in surface-to-volume ratio of nanoparticle and absorption of ligands. It affects the

electronic and magnetic structures at the surface and thus affects the magnetic properties of the material [37-38]. The magnetic anisotropy energy constant was increased with the reduction in particle size, due to the influence of surface anisotropy. At 0.2PUNCF, the size of self-assembled bead reduced which leads to enhance saturation magnetization by the impact of surface anisotropy. In elongated particles, the contribution of surface to the effective anisotropy leads to increase in the coercivity. The spin interactions are responsible for effective anisotropy which is contributed from shape anisotropy and surface magnetic spin [39]. Size effect and interconnected particles (0.2PUNCF) play a major to enhance the saturation magnetization and remanent magnetization rather than the increased particle size (UNCF) and elongated particles (0.5PUNCF).

Temperature dependent magnetization of UNCF, 0.2PUNCF and 0.5PUNCF at 100 Oe are shown in Fig. 4. Zero field cooled (ZFC) and field cooled (FC) curves of UNCF are shown in Fig.4a. Magnetic moment was decreased with increase in temperature for ZFC and FC (Fig.4a). At low temperatures the surface spin freeze in preferred orientation and moment saturate (0.012 emu/g) for ZFC in UNCF. However, at field cooled, the moment of UNCF was enhanced (0.0325 emu/g) could be rotation of the magnetization of the thermally hindered particles in the field direction. The trend followed the Curie's law for paramagnetic material where magnetization is affected by the temperature. The 0.5PUNCF sample showed similar trend as the UNCF sample where ZFC and FC decreased with increasing temperatures. However, the irreversibility in this sample was stronger than UNCF sample suggesting enhanced magnetic ordering in this system. On the contrary, 0.2PUNCF sample showed that the magnetization increased when the temperatures in increased up to 350 K. The FC curve followed Curie's law where magnetization decreased with lowering the temperatures. Similar trend was observed in superparamagnetic nanoparticles where sample showed hysteresis below blocking temperature [42-44]. At low temperatures (~32 K) of 0.2PUNCF (ZFC), the moment was decreased (0.0135 emu/g) may be due to blocking of particle moment in chaotic directions. The magnetic moment of 0.2PUNCF (ZFC) was enhanced with increase in temperature and it was saturated (0.0482 emu/g) above 350 K could be due to deliberate rotation of the magnetization of thermal hindered particles moment in the direction of field [40-41]. FC of 0.2PUNCF, the moment decreased with increase in temperature and at low temperature (5 K), it increased to 0.102 emu/g. On adding polymer (0.5 wt%) to Ni-Co ferrites, ZFC and FC were also reduced with increase in temperature. At low temperatures (~25 K), the moment of 0.5PUNCF was found to be 0.040 emu/g in both

ZFC and FC. Surface anisotropy in 0.2PUNCF sample leads to high magnetization and low coercivity consistent with the magnetic properties of superparamagnetic nanoparticles [42-48].

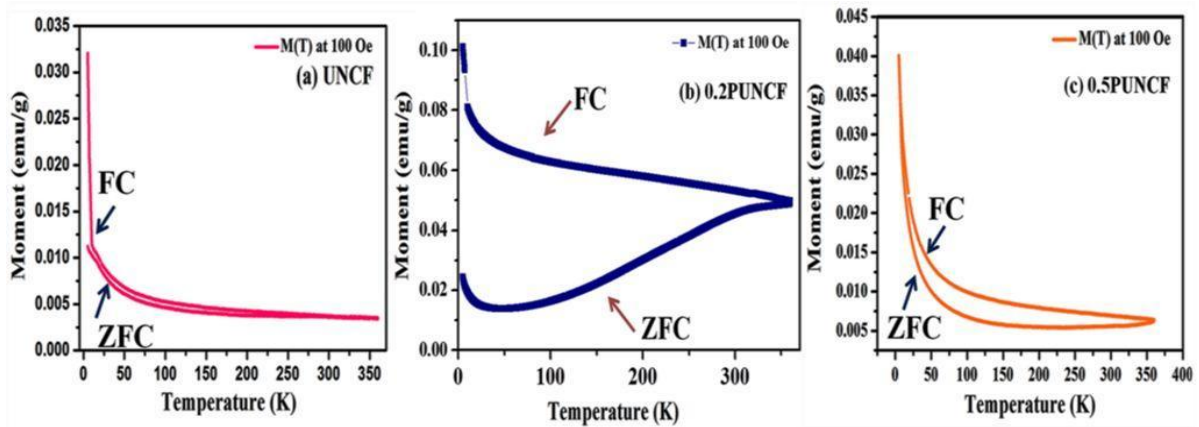


Fig.4. Zero field cooled (ZFC) and field cooled (FC) curves of (a) UNCF and (b) 0.2PUNCF and (c) 0.5PUNCF.

4. Conclusion

Magnetic polymer nanostructures of NiCoFe₂O₄/PVA have been prepared via an in-situ ultrasonication process. The samples were characterized by XRD, FTIR, Raman and SEM analyses respectively. In addition, magnetic properties were also investigated by VSM. XRD analysis confirmed the phase purity of Ni-Co ferrites (spinel structure). Reduced average crystallite size by 42.8% of Ni-Co ferrites was attained upon polymer incorporation. At 0.2 wt% of polymer, self-assembled beads of magnetic particles were observed whereas, for 0.5PUNCF, rectangle shaped was attained. Enhanced magnetic properties of polymer (0.2 wt%) incorporated in Ni-Co ferrite were observed due to size and shape anisotropy. The field and temperature dependent magnetization results showed superparamagnetic behavior in 0.2 wt% doped ferrite. Collectively, ultrasonication route is a simple, robust and cost-effective route to tailor the morphology of magnetic structures and creating size and shape anisotropy for enhancing magnetic properties. Hence, polymer based magnetic nanostructures could be useful in magneto-sensors and magnetic hyperthermia applications.

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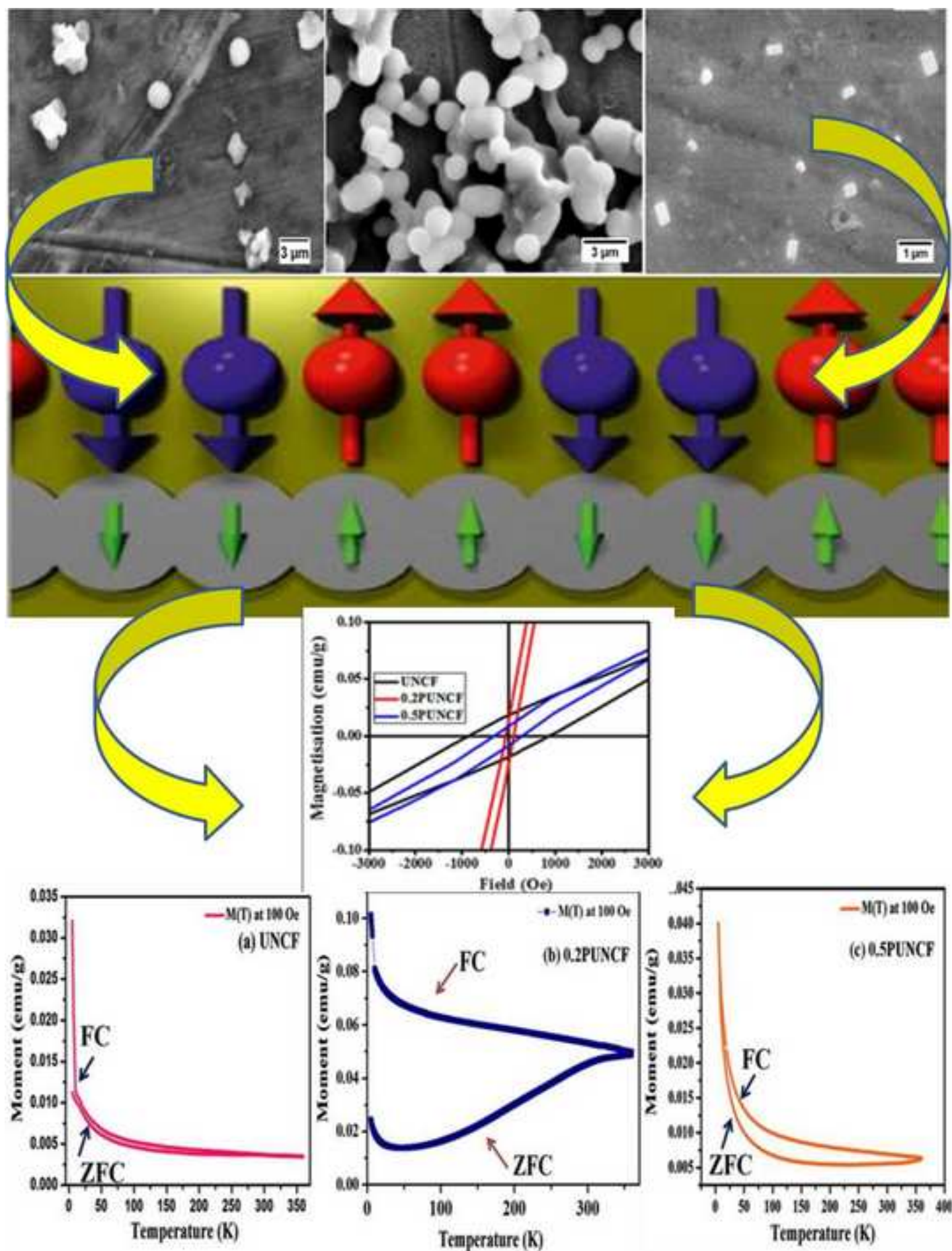
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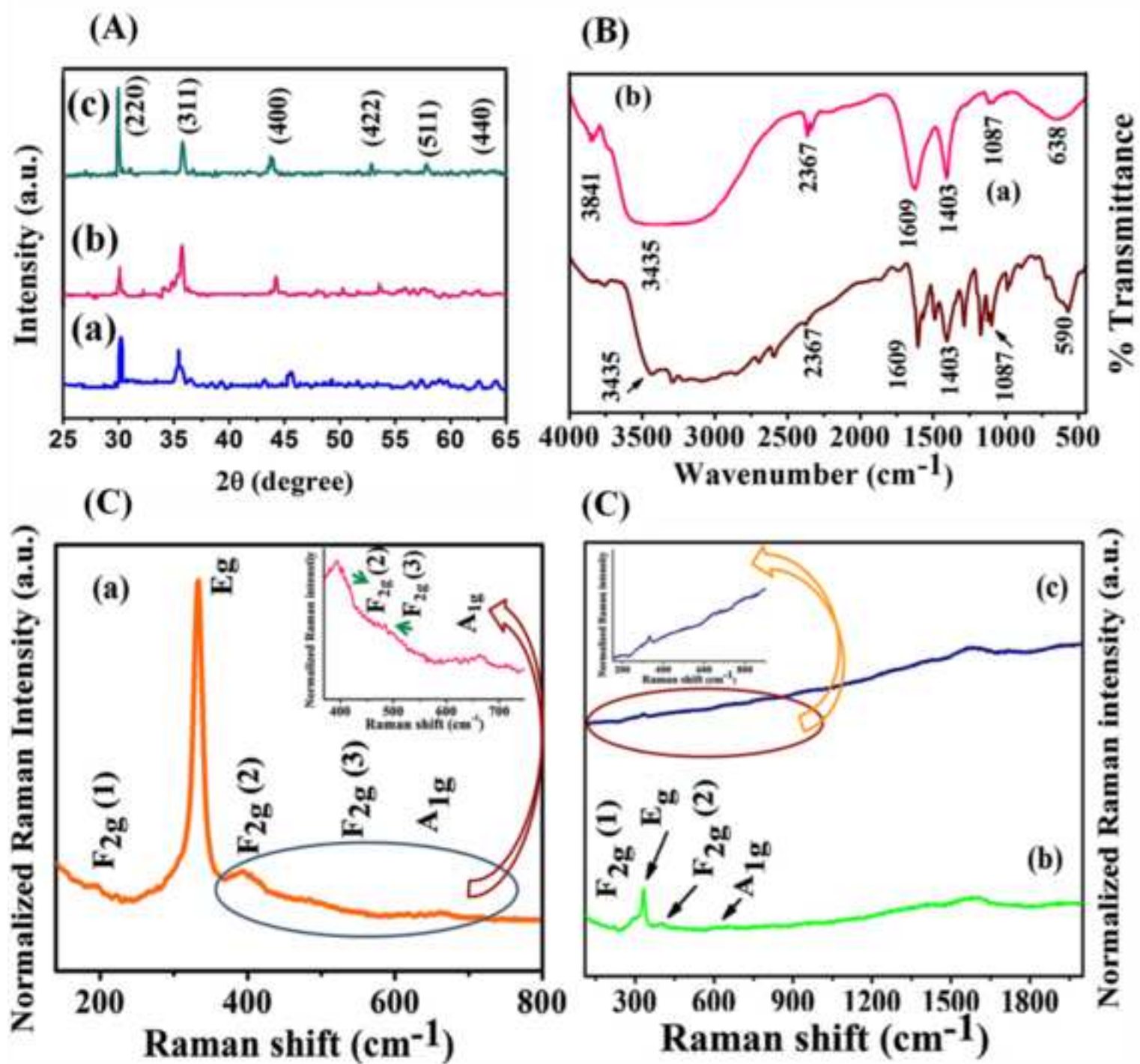
HIGHLIGHTS

- ❖ Ultrasonication Technique Simple Rapid and Effective for Polymer Nanocomposites (NCs)
- ❖ Ni and Co ferrites doped to Polymer NCs with Different Concentrations
- ❖ Polymer [polyvinyl alcohol (PVA)] (0.2g and 0.5g) added as a Surfactant to Ferrites Materials
- ❖ Phase purity of Ni-Co ferrites (spinel structure) confirmed by XRD, FTIR, Raman techniques
- ❖ Enhanced Saturation Magnetization of Polymer NCs Magnetic NPs Shape Anisotropy and Size
- ❖ Polymer NCs Magnetic Materials useful for future Magnetic-Sensor Applications.

List of table:**Table 1** Average crystallite size and lattice parameter of polymer based nickel and cobalt ions co-doped ferrites

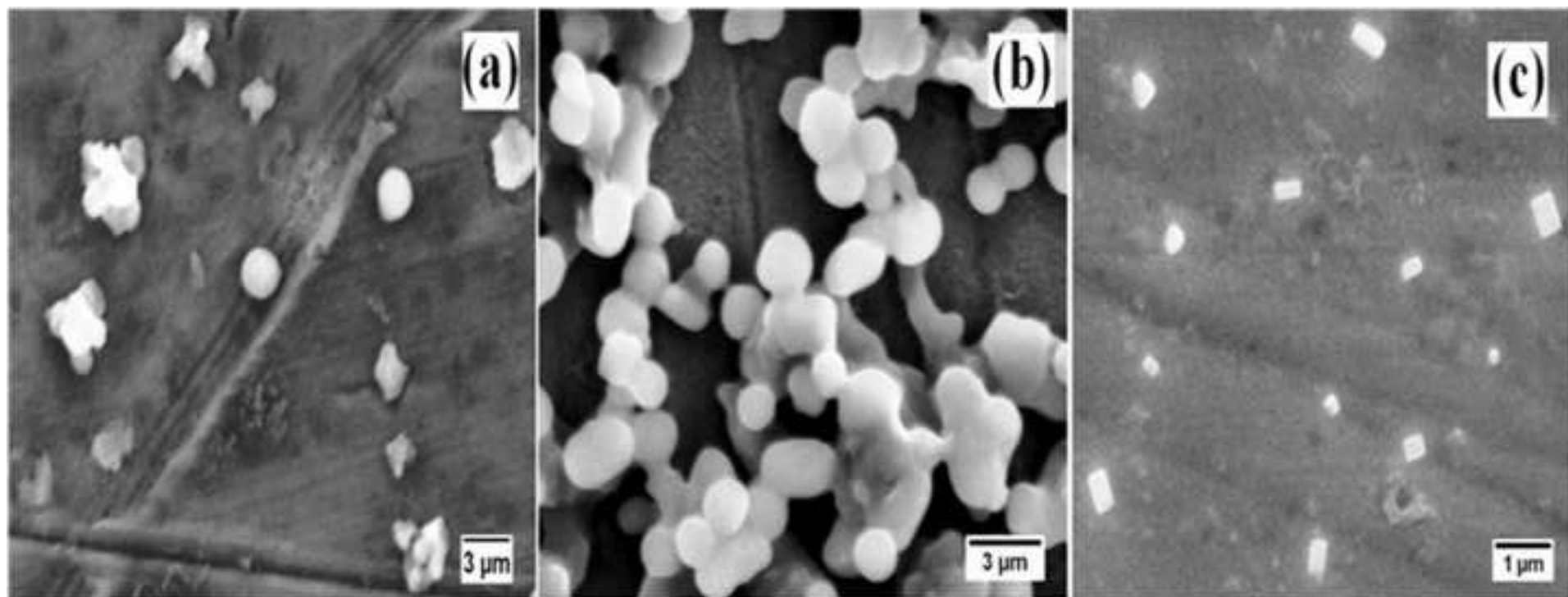
Sample code	Crystallite size (nm)	Lattice parameter a=b=c (Å)
UNCF	105	8.200
0.2PUNCF	60	8.000
0.5PUNCF	98	7.800

Figure

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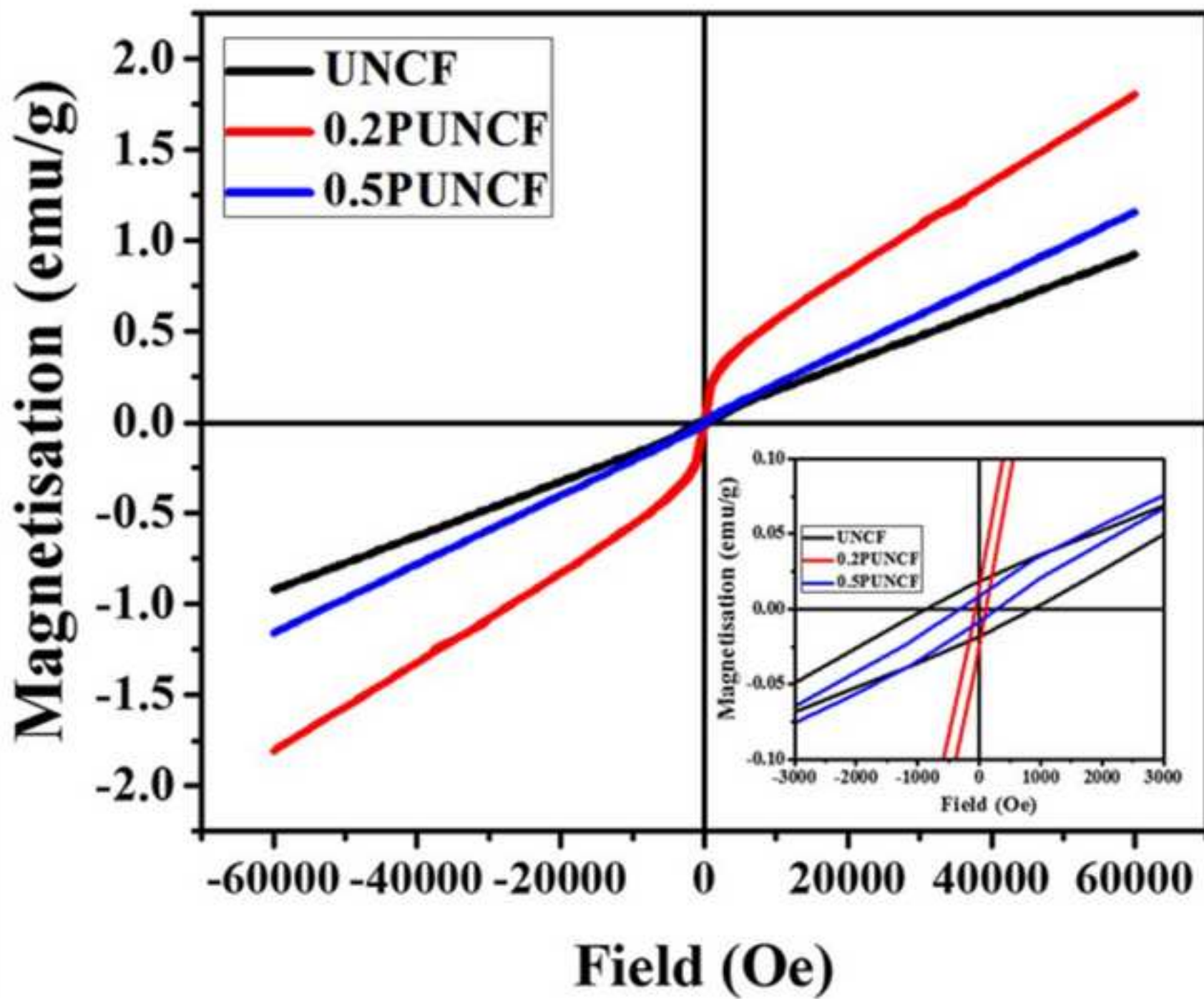
Figure

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