CHAPTER - 2
LITERATURE REVIEW

2.1 Introduction

The detailed background of the present research topic is reviewed, particularly on the synthesis, structural, dielectric and magnetic properties of the CSNPs are deliberated in this chapter.

2.2 Synthesis and Properties of Core-Shell Nanoparticles

In general, CSNPs are synthesised using a two-step process, first synthesis of core and second the synthesis of the shell. The synthesis techniques of CSNPs can be classified into two types depending on the availability of core particles: (i) The core particles are synthesised and separately encapsulated by the system with proper surface modification for coating the shell material [1, 2]. (ii) The core and shell particles are synthesised in the one pot method [3, 4]. In the first method, after the core particles are separately synthesised and purified by the successive washings and dried. Then they undergo proper surface modification for coating the shell material in the reaction mixture for shell formation. In the second method, the core particles are first synthesised using suitable reactants in the presence of a growth inhibitor and or surface modifier then after core formation is completed, more reactants are added to form the shell particles in the same pot [5, 6]. Consequently, the shell material is selectively deposited on the modified core surface and core-shell particles are formed. The basic advantage of external core synthesis is the fact that core particles are available in pure form and hence there is less possibility of impurities on the core surface. Whereas, in one pot synthesis, the main problem is that some impurity from the reaction media may be trapped between the core and shell layer.

The most important step during the synthesis of core-shell particles is to maintain uniform coating and to control the shell thickness. Several synthetic methods for core-shell particles have been reported by many research groups are precipitation, polymerization, microemulsion, sol-gel condensation, layer-by-layer adsorption techniques, etc. Here, we explained some recent reports regarding the CSNPs synthesis method.

Ji *et al.* [7] synthesised core–shell system of Cu/Fe_3O_4-SiO_2 microsphere through a two-step method. At first, the Fe_3O_4-SiO_2 microspheres were synthesised using the nano-Fe_3O_4 as the core, tetraethyl ortho-silicate (TEOS) as the silica source and cetyl trimethyl ammonium bromide (CTAB) as a surfactant. Secondly, the Cu nanograins obtained by reducing copper ammonia complexes with hydrazine hydrate supported on the surface of the Fe_3O_4-SiO_2 microspheres. The surface embedded Cu NPs act as an active sites for the low-concentration formaldehyde conversion to H_2 under mild reaction conditions. The agglomerations of the Fe_3O_4-SiO_2 CSNPs easily prevented by assemble the Cu NPs on the surface of Fe_3O_4-SiO_2 CSNPs. Liu *et al.*[8] developed the $FePt$-Fe_2O_3 CSNPs and then functionalized with polyethylene glycol (PEG). Folic acid (FA) conjugated on the surface of FePt- Fe_2O_3-PEG NPs for effective targeting of folate receptor-positive tumour cells. A doxorubicin (DOX) was loaded over the NPs using hydrophobic physical adsorption for targeted intracellular drug delivery and selective cancer cell killing. Magnetic resonance imaging (MRI) of $FePt$-Fe_2O_3-PEG NPs observed obvious tumour MRI contrasts both passive tumour accumulation and active tumour targeting of NPs with low toxicity for FePt- Fe_2O_3-PEG NPs.

Stefan *et al.* [9] introduced seed mediated growth method to prepare magnetite based CSNPs of Fe_3O_4-ZnS and Fe_3O_4-Au-ZnS. It consist a sequential growth of a

second or third component on a preformed magnetite seeds in the presence of sodium laurylsulphate additives. All the samples showed the superparamagnetic behaviour due to the nanoscale magnetite cores. Enhanced Photoluminescence and magnetization response were observed by inserting a gold shell between the magnetite core and ZnS outer shell. The Pd nanocrystals alternatively incorporated monodisperse core-shell like Fe_3O_4-C microparticles were synthesised by Fang *et al.* [10] using hard self-template method. The as-obtained system exhibited superparamagnetic characteristics. Mandal *et al.* [11] reported the formation of gold coated cobalt CSNPs obtained by a displacement reaction. Hysteretic magnetic properties of NPs depended critically on their overall size and the size of the magnetic core decreased as a function of the displacement reaction time.

Sun *et al.* [12] synthesised polyhedral Fe NPs with amorphous Al_2O_3/FeO_x composites shells by the arc discharge method. The shape of Fe NPs was quadrilateral, pentagon, hexagonal and sphere. The excellent electromagnetic (EM) properties were ascribed to the dielectric resonance from the special core–shell microstructure and the broad and strong natural resonance from the shape anisotropy of Fe NPs [12]. Wang *et al.* [13] fabricated Co coated Fe_3O_4 CSNPs by hydrothermal technique and electroless plating process. Due to the existence of the core-shell structure, the electromagnetic characteristic of the Fe_3O_4/Co NPs are exhibited in better microwave absorption performance and wider frequency band of microwave absorption than the pure Fe_3O_4 NPs.

The conductive polypyrrole (PPy) polymer nanocomposites (PNCS) reinforced with different magnetite (Fe_3O_4) NP were synthesised by Guo *et al.* [14] using surface initiated polymerization method. The Fe_3O_4/PPy PNCS exhibited the superparamagnetic behaviour. Lou *et al.* [15] reported a double-walled ellipsoidal or

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cocoon shaped α-Fe_3O_4 movable core for SnO_2 hollow shell NPs. These nonspherical hollow particles with movable magnetic cores were used for magnetically separable photocatalysts and self-assembled photonic crystals with controlled bandgaps. Dai *et al.* [16] developed a convenient and effective one-step pickering emulsion polymerization to synthesize temperature-sensitive core-shell multifunctional NPs. The size of these kinds of CSNPs could be controlled by the surrounding temperature. Lee *et al.* [17] recently showed that a mixture of different sized gold nanoshells in aqueous nanofluids would harvest a greater percentage of the solar spectrum than aqueous nanofluids containing solid aluminum NPs. They increased the efficiency of a direct solar receiver.

Liu *et al.* [18] prepared the FeNi/C NPs with graphite layers as shell and FeNi NPs as core and FeNi NPs coated with amorphous oxide by modified arc-discharge process. The influence of graphite layers on the microstructure, magnetic, thermal and electromagnetic characteristic of FeNi NPs were investigated. Compared with FeNi NPs, the lower saturation magnetization (M_s) of FeNi/C NPs was attributed to the smaller size. TGA and DTA showed graphite layers can help FeNi/C NPs to be stable securely below 240 ℃ in the air, while FeNi NPs were oxidized at about 90 ℃. The enhanced electrical resistivity of graphite layers arising from the special microstructure and defect properties when thickness was several nanometers, blocking the formation of an electric conducting network. This contributed to higher dielectric loss. Due to the magnetic particles separated by the graphite coating, the dipolar interaction was the main effect and exchange interactions were negligible in the FeNi/C NPs. The graphite layer protected the soft-magnetic properties of FeNi cores in the high frequency range as well as keep the l00 almost constant over 6–13 GHz. The graphite layer shell was responsible for increasing the magnetic/dielectric loss

and attenuation constant which leads to enhanced EM-wave absorption properties in the 9–18 GHz range.

Xia *et al*. [19] synthesised nickel coated silver bimetallic CSNPs by one-step reduction method. The core-shell structure had a prominent advantage in avoiding the aggregation of the NPs during the catalytic process. Yin *et al*. [20] demonstrated the one-pot synthesis method for the preparation of bifunctional Fe_3O_4-TiO_2 core-shell particles. The morphological results showed that 100–200 nm length and 10–20 nm diameters coated on the surface of 200–300 nm Fe_3O_4 submicrospheres. Reaction time, the titanium source had an influence on the morphology of core-shell particles. Gonzalez *et al*. [21] synthesised the Au-Ag bimetallic multi-shell NPs with the deposition of Ag on Au generated a pseudo-spherical geometry. Deposition of Au on Ag leads to the preferential formation of polygonal particles with sharp facet intersections. The final shape depended on the selection of the core metal. The optical properties changed with the shell coating. Initially, the gold colloid color was deep red; upon deposition of a silver shell, it turned yellow; a second hue. Finally, after the deposition of second silver shell, an orange color was observed. Wan *et al*. [22] developed a simple solution phase method to synthesis core-shell gold shell led to blue structured Fe_3O_4-ZnO NPs by one-pot sequential thermal decomposition of iron and zinc precursors in liquid polyols.

Recently, Wang *et al*. [23] and Choi *et al*. [24] reported the synthesis of uniform size and well crystalline nature CeF_3 and Gd_2O_3 based on CSNPs using polyol method. Although several researchers have attempted to control the thickness and uniform coating of the shell using several methods, controlling the synthesis parameter is very difficult. The main difficulties are (i) agglomeration of core particles in the reaction media, (ii) preferential formation of separate particles of shell

material rather than coating the core, (iii) incomplete coverage of the core surface and (iv) the control of reaction rate. Usually for core surface modification purposes, surface active agents [25] and polymers [26, 27] are often used by different research groups. These surfactants or polymers can change the surface charge and selectivity of the core particles. Resulting, the shell material can be selectively deposited onto the core surface to form uniform and completely coated core-shell particles.

2.2.1 Properties of Core-Shell Nanoparticles

There are various interesting properties of CSNPs, which are unseen in conventional metallic NPs, like tunable surface plasmon resonance and formation of SERS hot spots on a single NPs [28-30]. The magnetic core-metallic shell NPs exhibit both magnetic and plasmonic properties [31]. The effectiveness of the shell in the prevention of the iron-group metal core from oxidizing in air and from dissolving in acid environments is an important factor in the practical applications. Physical and chemical properties of the CSNPs will determine the application of these multifunctional materials. Klabunde et al. [32] found the important effect of the reactive shell such as Mg in core-shell systems. It prevented the oxidation of metallic magnetic core by the formation of a thin layer of MgO, which retained the magnetic property of the core even after long term exposure to air. Wuyou Fu et al. [33] analysed the oxidation temperature of Co core of Co/SiO_2 core-shell nanocomposite and proposed SiO_2 coating enhanced the resistance of cobalt particles against aerial oxidation.

Rai et al. [34] employed the $Au-Cu_2O$ CSNPs for CO and NO_2 gas detection. The better performance of $Au-Cu_2O$ CSNPs was mainly attributed to the pronounced electronic sensitization, high thermal stability and low screening effect of Au NPs. Mattei et al. [35] used the sol-gel technique for preparing the Au/NiO NPs embedded

in a porous silica matrix with a high specific surface area. They found these NPs increased the number of active sites for gas reaction and enhanced the sensor functionality. Sreenivasulu *et al*. [36] reported the induced polarization and magneto-dielectric effect in ferromagnetic-ferroelectric core-shell structured single phase multiferroics system showed permittivity and polarization in the range $1-5\%$ for fields in the order of 4 kOe. Skoropata *et al*. [37] analysed magnetic behaviour of γ-Fe_2O_3 core encapsulated within the Cu, CoO, MnO and NiO different shells by interaction through an interfacial layer of these CSNPs. The origin of the exchange bias and unexpectedly high overall anisotropy of the NPs is associated with the migration of shell ions into the vacancy site present in the surface layers of the core material.

2.2.2 Dielectric Properties of Core-Shell Nanoparticles

Great efforts have been made to develop core-shell nanocomposites with excellent dielectric properties and mechanical flexibility for the application of electric energy storage [38-41]. To prepare the high dielectric constant materials of the supercapacitors, different NPs (magnetic particles, high dielectric constant ceramic powders and conductive metal particles) have been encapsulated by the nonmagnetic and or ferroelectric polymer such as SiO_2, polyvinylidene fluoride (PVDF) and its copolymers respectively [42, 43]. When the percent of core NPs is up to the percolation threshold inside the shell boundary, the interactions between the core particles increased because of the formation of conductive network. High dielectric constant can be obtained when the fraction of the core is very close to not exceeding the percolation threshold. However, the dielectric loss also enlarges and it limits the practical application of these composites. Moreover, the enhancement of the dielectric constant is not far from satisfied degree, comparing with the increase of dielectric

loss. So, it is of great importance to maximize the dielectric constant and simultaneously minimize the dielectric loss for the practical application of the capacitors. It is known that the distribution of the core and the interaction between the core NPs and the shell matrix can greatly influence the dielectric performance of the composites. And the core NPs are prone to conglomerate into the secondary particle within shell matrix due to large specific surface energy and strong cohesion. Hence, numerous methods focusing on surface modification of the NPs have been developed to improve the dispersion of NPs in the shell matrix and the dielectric properties of the corresponding composites [44-46] resulting the surface modification of NPs can help to prevent agglomeration of the NPs and reduce the dielectric loss of core-shell based nanocomposites.

For nanocomposite materials, the interfacial regions between the inorganic filler and polymer matrix have profound effects on the dielectric properties and a variety of coupling agents used to modify the interfacial modulus [47, 48]. In this regard, Tanaka *et al*. [49] proposed a multicore model composed of a bonded layer, a bound layer, and a loose layer to describe the interactions of the components in a polymer nanocomposite dielectric. Few studies have reported the effect of the core-shell structure on the dielectric property in the core-shell nanocomposites. For example, Wei *et al*. [50] presented the dependence of dielectric properties of the composites with original and surface modified Co-ZnO CSNPs. Shen *et al*. [51] have reported an effect of Ag-C core-shell structure on dielectric properties of the Ag-C/polymer composites.

Li *et al*. [52] reported an effective layer-by-layer method for creating Al_2O_3 shells on the surfaces of high-ε $BaTiO_3$ and ZrO_2 NPs. The metallocene precatalyst [rac-ethylene-bisindenyl] zirconium dichloride is chemisorbed and activated by

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Al$_2$O$_3$-encapsulated NPs having core-shell structures. Polymerization of propylene by the catalysts anchored on the CSNPs then affords nanocomposites with the filler well-dispersed in the polyolefin matrix. The moderate permittivity of the Al$_2$O$_3$ layer greatly suppresses leakage currents and dielectric loss in these nanocomposite materials [65]. Berthelot *et al*. [53] further evidenced the low dielectric loss core–shell structured BaTiO$_3$-MgO NPs synthesised by combining thermolysis and fast sintering approaches. The electron microscopy study evidenced a shell composed of randomly oriented MgO nanocrystallites. The composite effect leads to significant modifications in both the dielectric properties and Curie–Weiss parameters compared to uncoated BaTiO$_3$, especially a decrease and thermal stabilization of both the permittivity and the dielectric losses. The Ag-TiO$_2$ CSNPs filled ferroelectric poly(vinylidene fluoride) (PVDF)-based composites were prepared to study the effect of core-shell structure on dielectric permittivity in the Ag-TiO$_2$/PVDF nanocomposite by Dang *et al*.[54]. Dielectric measurements showed the shell-layer thickness of the Ag-TiO$_2$ CSNPs played a key role in deciding the final values of the dielectric properties of the nanocomposite. The variation of dielectric properties of the nanocomposites with temperature also depends on the shell-layer thickness of the Ag-TiO$_2$ CSNPs.

Balasubramanian *et al*. [55] reported a route to grow core–shell structured nano-particles (paraffin@TiO$_2$) by thermal evaporation technique. The paraffin acts as matrix and also prevents the nanoparticle from aggregating. The core–shell structured TiO$_2$–paraffin NPs showed low dielectric loss in the frequency range of 100 Hz to 1 MHz. The observation made by Guan *et al*. [56], multidielectric polarization of Co/graphite CSNPs with enhanced dielectric losses and magnetic losses at microwave range. It is not observed in any carbon related materials or Co

NPs. Theoretical simulation showed this phenomenon is associated with the core-shell architecture. Bowler *et al*. [57] reported the core-shell heterogeneous structures with the different resistivities showing high permittivity due to interfacial polarization phenomenon between the core-shell regions. Nanocomposite comprising a poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP) polymer matrix and $BaTiO_3$-TiO_2 core–shell structured NP fillers were prepared by Rahimabady *et al*. [58], the dielectric constant of the core-shell particles was greater than three times higher than that of the nanocomposite without the TiO_2 shell layer. The significant improvement in electric polarization is attributed to the highly interactive interfaces among the multiple dielectric materials with the introduction of the intermediate TiO_2 layer. It improved the breakdown field (>340 MV m^{-1}) and dielectric energy density of 12.2 J cm^{-3} was achieved among the highest energy densities for polymer–ceramic composites.

Hydrothermally prepared ferrite/perovskite core-shell systems like, Fe_3O_4/$PbTiO_3$, γ-Fe_2O_3/$PbTiO_3$, γ-Fe_2O_3/$Pb(Zr,Ti)O_3$, $CoFe_2O_4$/$BaTiO_3$, $CoFe_2O_4$/$PbTiO_3$ and $CoFe_2O_4$/$Pb(Zr,Ti)O_3$ showed strong interactions between the core and shell materials and the ferroelectric layer dramatically affected the crystal structure, resistivity and magnetic properties of the composites explained by Liu *et al*. [59]. Xie *et al*. [60] observed the larger dielectric constants of well-defined core–shell structured $BaTiO_3$–PMMA nanocomposite compared with pure PMMA. Higher dielectric loss could be observed in the very low frequency/high temperature range. Cobalt ferrite/barium titanate NPs with a core-shell structure were synthesised by combining co-precipitation and organosol methods (Etier *et al*. [61]). Dielectric and magnetic properties of the particles were studied using impedance and Mössbauer spectroscopy. This combined co-precipitation and organosol methods are promising for fabrication

of multiferroic ceramics with the core-shell structure. Chemically gel-derived silica glass composites of copper core–copper oxide shell NPs prepared by Basu *et al*. [62]. Detailed modulus spectra of these core-shell particles indicated the wide distribution of relaxation times in the interfacial amorphous phase as compared to that of original glass. This clearly brought out the difference between the glass medium and the interfacial amorphous phase generated in the nanocomposites.

2.2.3 Magnetic Properties of Core-Shell Nanoparticles

Core-shell NPs with magnetic components have attracted much interest in both fundamental research and practical applications. In magnetic CSNPs, the novel properties of magnetic components can be combined with those of another active component to make bifunctional or even multifunctional NPs. Many fundamental but critical properties of these CSNPs are still not well understood. Due to the unusual multiphase polycrystalline structure of the NPs, it favours the noncollinear arrangement of the magnetic moments and to the highly disordered magnetic surface layers from the high specific surface area, the CSNPs exhibit anomalous magnetic behaviours. The positive or negative effect also depends on the core–shell materials. In the Ag coated Co NPs, coercivity (H_c) and remanence (also called remnant magnetization, M_r) at room temperature are weak and no magnetization is saturated even at a field of 1tesla [63]. The blocking temperature (T_B) of NPs with a magnetic core and a nonmagnetic shell is mainly determined by the size of the magnetic core [64]. The slightly reduced T_B in ensembles of core-shells, compared to pure magnetic NPs of the same size as the magnetic core is attributed to the increased spacing (decreased interaction) between magnetic cores [65].

An interesting magnetic nanoparticle system is that of core-shell structured NPs in which the magnetic core is coated with a layer of a non-magnetic,

antiferromagnetic, or ferro/ferri-magnetic shell. The coating of shell layer over the core leads to exchange bias (a shift of the hysteresis loop along the field axis) and improvements in the thermal stability of the core [66, 67]. Magnetic properties of CSNPs contains both magnetic and non magnetic system is less studied yet more interesting due to particle at nanoscale, ferromagnetism arises from magnetic moments created by cation or anion defects on the surface of the NPs [68].

The relative dimensions of core-shell thickness and chemical composition are the crucial parameters to tailoring the magnetic properties of FePt NPs coated with MFe_2O_4 shells such as Fe_3O_4 and $CoFe_2O_4$ reported by Sun *et al*. [69]. Chen *et al*. [70] synthesised Ni-Au CSNPs through a redox-transmetalation method in reverse microemulsion. The magnetization curves at 300 K showed the typical superparamagnetic behaviour with the saturation magnetization 0.7 emu/g. Mori *et al*. [71] developed Ruthenium-hydroxyapatite-encapsulated superparamagnetic γ-Fe_2O_3 nanocrystallites by chemical method. Monomeric Ru cation species containing Ru (IV) species were uniformly fixed on the outer HAP surface. The RuHAP-γ-Fe_2O_3 shows highly efficient heterogeneous catalyst system for the oxidation of alcohols using molecular oxygen. Recovery of the catalyst was facilely accomplished by external application of a permanent magnet. Zhao *et al*. [72] synthesised γ-Fe_2O_3-hydroxyapatite (HAP) CSNPs by chemical method and analysed interaction of core and shell material by Mossbour spectroscopy. The γ-phase Fe_2O_3 core is thermally stable up to 600 °C by coating of HAP shell. They found the strong interaction between HAP and nano iron oxide particles surfaces and the interaction imposed by HAP stabilize the size and crystal phase of γ-Fe_2O_3. During the heat treatment, the interaction imposed by HAP produce large amounts of distorted octahedral coordination Fe sites in the interior lattice that gives strong magnetic properties.

Zhu *et al*. [73] reported a facile thermo decomposition process of magnetic graphene nanocomposites with core-double shell NPs. From the high-resolution transmission electron microscopy and energy filtered elemental mapping they observed a core-double-shell structure of the NPs with crystalline iron as the core, iron oxide as the inner shell and amorphous Si−S−O compound as the outer shell. These magnetic CSNPs demonstrated in extremely fast Cr (VI) removal from the waste water with high removal efficiency and with an almost complete removal of Cr (VI) within 5 min. The large saturation magnetization (96.3 emu/g) of the synthesised NPs allows fast separation of the magnetic particle from the liquid suspension.

Clusters of a Co core with a noble metal shell studied by Guevara *et al*. [74] and Wang *et al*. [75] with theoretical calculation using a parameterized tight-binding model and a spin-polarized s–p–d tight binding model and it was predicted that the noble metal (Cu) develops a net polarization that changed the total magnetic moment of the clusters. It was predicted that the size, shape and materials of the shells have an effect on the magnetic properties. Thus, the magnetic properties of the Co NPs expected to differ from those of Co NPs with a noble Au or Cu shell. Wiedwald *et al*. [76] found that the ratio of orbital-to-spin magnetic moment enhancement of 300% in 11.4 nm Co magnetic NPs due to an increment of orbital magnetic moment at the strained interface between the antiferromagnetic CoO shells 2-2.5 nm formed over the metallic ferromagnetic Co core 7-8 nm.

The magnetic order and temperature dependence of the magnetic moment in the doubly inverted core-shell MnO/γ-Mn$_2$O$_3$ system were associated with the magnetic proximity effect. An induced magnetic magnetic moment in the γ-Mn$_2$O$_3$ shell persists above its T_c due to the exchange coupling with the MnO core explained by Golsovsky *et al*. [77]. Exchange bias is typically attributed to the unidirectional

coupling between ferromagnetic (FM) and antiferromagnetic (AFM) layers but can also existed in the samples having a ferromagnetic domain, spin glasses, or disordered surface spins [78-80]. It is observed from the studies by Ong *et al*. [81] in the Fe/Fe_3O_4 CSNPs the frozen interfacial spins increased the total magnetic moment and also it mediates a strong exchange coupling between the core and shell domains under field-cooled conditions. Zeng *et al*. [82] synthesised bimagnetic $FePt/MFe_2O_4$ M=Fe,Co CSNPs via high-temperature solution phase coating of 3.5 nm FePt core with controlled MFe_2O_4 shell thickness of 0.5 to 3 nm. An assembly of these CSNPs showed a smooth magnetization transition under an external field through effective exchange coupling between the FePt core and the oxide shell.

The coercivity of the $FePt/Fe_3O_4$ particles depended on the volume ratio of the hard and soft phases. Chandra *et al*. [83] observed that the $Fe/\gamma\text{-}Fe_2O_3$ CSNPs exhibited collective super spin glass-type behaviour below the glass transition temperature. The exchange bias phenomena were depended on the magnetic state of core and shell material. Exchange bias was developing at the temperature that marked the onset of shell blocking below the freezing temperature of the core. The core and shell material in the $CoFe_2O_4/CoFe_2$ CSNP couple through the exchange-spring mechanism at the optimum shell thickness is 8.0 nm. The critical thickness of the soft phase shell material is the most relevant parameter to determine the exchange-spring regime reported by Soares *et al*. [84].

The unusual exchange bias phenomenon has been observed in $BiFeO_3$ core and $NiFe_2O_4$ shell NPs both zero field cooled (ZFC) and field cooled (FC) hysteresis loops at 5 K by Yusuf *et al*. [85] further evidenced the exchange coupling phenomenon in CSNPs from the FC hysteresis loops exhibited an enhancement of the remanence and a decrease in the coercivity as compared to the ZFC. The observed

features indicated the presence of an interface exchange coupling between $BiFeO_3$ core and $NiFe_2O_4$ shell. $BiFeO_3/NiFe_2O_4$ multiferroic/ferromagnetic composite system showed a magnetic ordering even at room temperature.

Evans et al. [86] further evidenced the exchange-bias effects in CSNPs of ferromagnetic (FM)-aniferromagnetic (AFM) CSNPs at the roughened core-shell interfaces. The magnitude of the exchange-bias field was strongly correlated with the net interfacial moment in the antiferromagnet and it was proportional to the degree of the interfacial roughness and not by a value of the AFM anisotropy. Soares et al. [87] analysed the exchange-bias and exchange-spring coupling in magnetic CSNPs at low temperature. The magnetic hysteresis loops were found to be strongly influenced by the thickness of the $CoFe_2$ phase. A strong exchange-spring coupling was observed for samples with thickness of the order of 8 nm or higher. Below this critical value the core and the shell are weakly coupled. The presence of exchange-bias field is strong evidence that exchange-type interactions occur in nanostructured core–shell systems. Iglesias et al. [88] reported the microscopic origin of exchange bias of individual CSNPs by Monte Carlo simulations and they concluded that the existence of a net magnetization due to uncompensated spins at the shell interface is responsible for the exchange coupling across the core/shell interface. It led to an enhancement of exchange bias in core/shell nanosystem.

Lai et al. [89] analysed the magnetic property of NP Ag core with Fe_3O_4 shell synthesised by polyol method. They found that too small Fe_3O_4 shells volume resist thermal fluctuation and these NPs showed the superparamagnetic behaviour above blocking temperature of 100 K. Exchange-bias coupling occurred in field-cooled hysteresis loops. Sun et al. [90] and Hu et al. [91] studied the CSNPs with FM (core)/AFM (shell) and Inverted AFM (core)/FM (shell) to explain the exchange bias

(EB) arising from the core-shell structure and they concluded the reason for the EB is the freezing of interfacial spins or the growth of droplets with uncompensated spins.

Wen *et al*. [92] observed the greatly enhanced coercivity of Au core-Co shell NPs at 10 K, compared to the pure cobalt sample is due to the pinning effect of cobalt spins at the Au/Co interface. The pinning mechanisms include strain pinning and demagnetizing field pinning. Kumar *et al*. [93] used ferromagnetic resonance spectroscopy (FMR) to study the electromagnetic properties of gold coated Fe_3O_4 CSNPs as well as uncoated Fe_3O_4 NPs. They observed that the core-shell ferrites exhibit multiple resonance modes. EPR study of ultrafine Mn-Zn ferrite particles dispersed in solid kerosene was investigated by Nagata *et al*. [94]. The resonance fields shift of EPR spectra for the partially oriented particles were proportional to the second powers of the linewidths and for the particles were randomly oriented, the shift behaved as third powers of the linewidths. Zyser *et al*. [95] analysed the ultra small Fe_2O_3 particles dispersed in an Al_2O_3 matrix by EPR measurement. The resonance field shift of EPR spectra was proportional to the second powers of the linewidths, implied the super paramagnetic nature of the particles.

2.2.4 Structural Characterisation

The characterisation of CSNPs is critical owing to the presence of shell material on the core surface. This necessitates a suitable characterisation technique is always required for both the core and shell. Most characterisation techniques used are the same as those used for single particles and one technique may not be sufficient. The most significant characterisation techniques used for CSNPs are those for the measurement of size, shell thickness, elemental and surface analysis, optical properties, and thermal stability among others. Conventional characterisation techniques such as X-ray diffraction (XRD), transmission electron microscopy (TEM)

and UV -Visible spectroscopy are the ones most often used. Depending on the characterisation techniques and different instruments, structural analyses of CSNPs are described in the following sections.

Powder X-ray diffraction is also extensively used for the characterisation of synthesised crystalline materials. It is used mainly for the identification of unknown materials and to characterise the crystallographic structure, crystalline size (grain size), and preferred orientation in polycrystalline or powder solid samples. The effect of finite crystallite sizes as measured by the broadening and intensity change of the peaks in X-ray diffraction is explained by the Scherer"s equation. For CSNPs, it is an indirect proof of the presence of a complete uniform coating. Because of the coating on the shell materials, the diffraction peak intensity of the core material decreases [3, 96] and after a sufficient thickness is laid down, the peak completely disappears. The low intensity diffraction peaks of the core material can appear after the coating but this may be due to insufficient shell thickness and the amorphous nature of the shell material [97-99].

Transmission electron microscopy (TEM) provides much more important information about the confirmation of core-shell formation through contrast difference, overall particle size, core size, shell thickness, uniform or nonuniform shell coating, lattice fringes of the shell material, etc. From the contrast difference of the core and shell material, the size and morphology of the particles can be easily measured. For much higher magnification, capable of seeing resolution even at the molecular level, HR-TEM (high-resolution TEM) is used [100]. Images yield information on crystallinity, lattice fringes, and even the d-spacing of the core-shell materials.

Optical properties are extremely sensitive to any nanocrystal surface

modification consequently, they can give some indirect ideas about the coating of the shell materials on the core surface. UV-Visible spectroscopy is a common spectroscopic technique used in the analysis of different types of NPs. In particular, those with energy absorption capacity in the UV-Vis region give an absorbance spectrum in this region. In CSNPs characterisation, UV-Vis is used to compare the individual spectra of core, shell and core/shell material. In the UV-Vis spectra, the intensity (absorbed or emitted light) and peak wave lengths will be changed after coating. In addition, by increasing thickness of the shell material, the intensity and peak wave lengths are shifted toward those of the pure shell materials [101]. However, UV spectroscopy provides indirect support for the shell material coating on the core surface.

Bochicchio *et al*. [102] analysed the structural instability of core-shell nanosystem. They found the optimal shape and placement of the core in CSNPs strictly correlated to the overall geometry of the NPs. The core very often tends to approach the NPs surface is the lowest energy configuration. Experimentally grown centered cores are metastable structure due to the aging problems which causes more asymmetric shapes of core in core-shell nanosystem. Morphological instability of CSNPs and its evolution in different environments were studied by Pedersoli *et al*. [103] through coherent diffraction imaging (CDI) technique and they compared the experimental results with simulated diffraction patterns for clustered Co-SiO$_2$ CSNPs with 10 nm core diameter and 30 nm shell outer diameter. They confirmed their ability to resolve the mesoscale morphology of complex metastable structures. Single-shot diffractive imaging can be used to explore the evolution of the spatial composition and structure of complex nanostructures exposed to different ambient conditions. Chung *et al*. [104] prepared the Fe-Au CSNPs via the microemulsion

process and its surface grafted with methotrexate anticancer therapeutic and indocyanine green fluorescent. The in-vitro experiments showed that the NPs were biocompatible; nonetheless, the Fe-Au-PSMA-ICG/MTX NPs killed cancer cells via the magnetic hyperthermia mechanism and the release of methotrexate.

Portales *et al*. [105] and Cazayous *et al*. [106] have quantitatively interpreted the Raman scattering of CSNPs and they concluded the vibrational dynamics of core-shell nanostructures depends crucially on the coupling between the shell and core materials. For the Ni-Ag CSNPs due to the weak bonding between Ag and Ni atoms, shell material peak only observed. In the case of Cu-Ag CSNPs, both core and shell materials peaks were observed due to the good phase matching of the acoustic wave between shell and core materials. Suryanarayanan *et al*. [107] investigated the porosity of titania and zirconia covered Ag and Au the metal core reactivity as a probe. The presence of pores was confirmed by the reaction between halocarbons and CSNPs. In CSNPs the core got converted into ions, which are leached out through the shell. Halocarbons having different alkyl chain lengths reacted with metal cores at different rates due to the differences in the accessibility of the core. The electrochemical accessibility of the core could be reduced by blocking the pores by adsorbates. With the adsorbed dye molecules on the oxide shell, metal cores were stable for extended periods of time even after the addition of halocarbons. The porosity of different kinds of shells was largely similar allowing molecular and ion penetration.

2.3 Conclusions

The CSNPs have been summarized in details. There are different core-shell materials available. It was found from literature that metal oxide based CSNPs have a wide range of application in real life as it is more stable and inert. Many methods are available for synthesis of core-shell nanocomposites. The polyol and co-precipitation method is the simpler one as these methods are very useful and the isolation of particles is easy. Relatively few reports have been published on the magnetic and dielectric properties of CSNPs. Thus, in this study, fabrication of core-shell nanostructure containing magnetic and non-magnetic system and their dielectric and magnetic properties are investigated and presented.

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