Mössbauer spectroscopic investigations on iron oxides and modified nanostructures: A review

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Pure and doped iron oxide and hydroxide nanoparticles are highly potential materials for biological, environment, energy and other technological applications. On demand of the applications, single phase as well as multiple phase of different polymorphs or composites of iron oxides with compatible materials for example, zeolite, SiO2, or Au are prepared. The properties of the as-synthesized nanoparticles are predominantly dictated by the local structure and the distribution of the cations. Mössbauer spectroscopy is a perfect and efficient characterization technique to investigate the local structure of the Mössbauer-active element such as Fe, Au, and Sn. In the present review, the local structure transformation on the optimization of the magnetite coexisted with iron hydroxides, spin dynamics of the bare, caped, core–shell and the composites of iron oxide nanoparticles (IONPs), dipole–dipole interactions and the diffusion of IONPs were discussed, based on the findings using Mössbauer spectroscopy.

Introduction

Iron oxide (IO) are known to the human kind since centuries. It is yet one of the widely studied nanoparticles which has rapid development in nanotechnology due to its indispensable and superior properties in many applications [1–5]. Iron (Fe) is one of the most abundant transition metals on earth crust. Therefore, it can be the backbone of the nanotechnology and development to a great extent [6]. Iron oxide nanoparticles (IONPs) are widely used in various applications such as biomedicine, magnetic storage media, water treatment, electrochemical energy storage, and catalysis [7–10]. The large surface-to-volume ratio of IONPs which is a custom to surface energy plays an important role in maintaining stability, chemical compositions, and lattice constant [11]. The polymorph transition of IONPs is also an interesting aspects as it widens the scope of application by the same material with low cost and safe energy and time. However, there are some major challenges for IONPs as they oxidize very easily when exposed to normal atmospheric environment and thus there is a stability issue. To counter this problem, there is need for some capping agent to modify the surface without affecting the structure as a protective agent. Exploring other materials along with IONPs are very essential and could give new ideas and understanding in the field of IONPs. There is always room to explore more in this field as there is possibility of constructing a nanohybrid IONPs which can possess multifunctional properties of magnetic as well as biological or any other functions, making it one of the most promising nanomaterials. It is reported [12] that the magnetic response of IONPs can be enhanced with a change in morphology (surface anisotropy) and the effective anisotropy can be enhanced by exchange of coupling that altered the magnetic response.

Superparamagnetic behaviour of IONPs which is strongly dependent on size of the IONPs is also one of the important aspects for magnetic nanoparticles [11]. They are introduced extensively in the field of magnetic resonance imaging (MRI), drug delivery, and hyperthermia [13–16]. For example, at early stage of tumour, it is hard to detect using MRI equipment only because of the limitation in its sensitivity. The signal intensity can be enhanced using superparamagnetic iron oxides (SPIO) as contrast agents [13]. In addition, some biomedical research using nanoparticles requires the need of small particle size distribution and surface coating for biocompatibility [13, 14]. In
this regard, SPIO nanoparticles will be helpful and can be utilized through surface modification for biocompatibility. Thus, most work in this field is to improve the biocompatibility of SPIO nanoparticles by controlling shape, size distribution and its surface.

Here, we highlighted some of the applications that are widely studied recently. Oluwasanmi et al. [17] prepared hybrid core–shell gold-coated iron oxide nanoparticles through the use of microfluidics. It is found to be superior method for manufacturing hybrid nanoparticles from uncoated IONPs. Belén Cortés-Llanos et al. [18] reported the effect of coating and size of IONPs in the magnetic resonance imaging (MRI). They have prepared IONPs with inorganic core and different coatings to examine the aggregation and interactions in the physiological media together with cell levelling efficiency. They found that IONPs (without coating) suspended in biological media undergo adhesion of molecules and partial removal of coatings. In addition, IONPs with the core size of 14 nm and coated with DMSA was found to attend the highest rate and a coefficient by MRI measurement. Overall, they have provided a way to improve the contrast in MRI which gives advantage to biomedical applications. Anoud Alkhayal et al. [19] have prepared cubic superparamagnetic iron oxide nanoparticles (SPIONs) with reduced graphene oxide (rGO) nanocomposites using microwave emulsion method. They have controlled the shape and size of the nanoparticle through reaction time, pressure, and power. In addition, to enhance the biocompatibility, SPIONs/rGO nanocomposites were coated with polyethylene glycol (PEG). They employed the SPIONs/rGO/PEG nanocomposite to magnetic hyperthermia, obtaining a promising specific adsorption rate (SAR) value of 58.33 W/g in acidic solution. Ramos-Guivar et al. [20] reported a critical review on the removal of heavy metals mainly As and Pb using IONPs. They highlighted that the adsorption of As and Pb clarify mainly with the use of techniques like Zeta potential, in-field Mössbauer spectroscopy, XPS, etc. Ali Dheyyab et al. [21] have reported a review highlighting the importance of the gold-coated IONPS in biomedical applications due to its oxidation resistance, chemical stability, and unique optical properties. IONPs/Au nanocomposites have been widely regarded as therapeutic agents for its applicability in hyperthermia, catalysis, MRI, drug delivery, and protein separation. However, they suggested that the use of IONPS/Au nanocomposites as medical agent is still in its early period and there is lot to incur for its development. Talking of the protein separation properties, recently Y asmin Abo-Zeid et al. [22] have examined a docking method. They have controlled the shape and size distribution of such material can be classified into two different categories and studied using Mössbauer spectra at 300 K. (i) If the Mössbauer line shape has a broad spectrum, the Mössbauer spectra may have a combination of relaxed superparamagnetic doublet and magnetic components. The blocking temperature of such IONPs will be usually above 300 K [20, 26]. (ii) If the Mössbauer line spectra show only strong relaxed component, i.e., only doublet in a superparamagnetic regime, then a relatively narrow particle size distribution can be observed. In addition, such materials exhibit weak or negligible interparticle interactions. The blocking temperature for such IONPs will be below 300 K [27]. This being said the blocking temperature is dependent on the effective magnetic anisotropy constant and also the mean volume of the particles [28]. Moreover, zero-field Mössbauer spectra at 300 K can hardly distinguish between nanomagnetite and nanomaghemite for which size are at superparamagnetic regime (below ~10 nm). To overcome this issue, low temperature and in-field Mössbauer spectroscopy are required. Recording the Mössbauer spectra in a wide range of temperatures will give us a better understanding in the magnetic behaviour of the IONPs, including the magnetic transition temperatures [20, 29]. There is a possibility of detecting not only those transitions associated with loss of magnetic ordering, i.e., Neel temperature (temperature above which antiferromagnetic materials becomes paramagnet) and blocking temperature (temperature below which material shows slow relaxation of magnetization) when a sextet is changed to doublet in the spectra. The importance of temperature could be address with an example of IONPS at room temperature. The spectrum of bulk Fe_{3}O_{4} NPs consist of two sextet from octahedral and tetrahedral with different hyperfine field and isomer shift indicating the oxidation state of Fe. But, in a superparamagnetic Fe_{3}O_{4} NPs, the sextets collapse to a single doublet and therefore, the tetrahedral, octahedral Fe, and their corresponding oxidation state could not be identified. To resolve this issue, the sample temperature is needed to be brought below the blocking temperature. Below the blocking temperature, the doublet will transform to sextet. If the sextet is still not resolved, an external magnetic field is required. The Fe at different sites will respond differently to the external magnetic field, resulting in the resolution of the superposed sextets.
It can detect the Verwey transitions of Fe₃O₄ at low temperature of ~120 K where a cubic inverse spinel structure is changed to monoclinic crystal structure [30]. It can also detect the transitions associated with the change in magnetic ordering such as change from antiferromagnetic to weak ferromagnet in the case of hematite (α-Fe₂O₃) at Morin temperature ~260 K (temperature below which the antiferromagnetic ordering in hematite is reorganized from being aligned perpendicular to the c-axis to be aligned parallel to the c-axis) [29]. This change is demonstrated by the change in the Mössbauer parameters mainly by the quadrupole shift. In addition, in the case of external applied field, the corresponding magnetic moment are aligned in the direction of external field, thereby resolving the magnetic relaxation process and interfering Fe atoms coordination and spins [20]. Thus, a difference in the Mössbauer parameters will arise and one can separate the contributions of each site through the proportion of relative absorption areas. Another benefits of implementing in-field Mössbauer experiment is that it can provide the canting angles and fractions of Fe spins on the particle surfaces. These canting angles are directly related with the quadrupole shift [29]. Mössbauer spectra of synthetic hematite (α-Fe₂O₃) at RT give hyperfine parameters of δ (isomer shift) = 0.37 mm/s, Δ (quadrupole splitting) = −0.21 mm/s and B (Hyperfine field) = 51.7 T [29]. While that of nanostructured magnetite gives δₐ (teta) = 0.34–0.36 mm/s, Δₐ = 0.04 mm/s, Bₐ = 45.6–48.7 T and δₐ (oct) = 0.36–0.37 mm/s, Δₐ = 0.07 mm/s, Bₐ = 41.1–43.8 T [31, 32]. These parameters can be used to identify the phase of hematite and magnetite in the samples.

While standard Mössbauer spectroscopy is a lab-based technique that uses a radioactive ⁵⁷Fe source to generate the resulting γ-rays, the technique can also be performed at selected synchrotrons. The higher local resolution and shorter measurement time available with synchrotron-based Mössbauer spectroscopy is a significant advantage [33]. Interestingly, Mössbauer spectroscopy has also been employed to study the soil in Mars using miniaturized Mössbauer spectrometer which has been installed in the Mars rover [34–36]. It is also used for geotechnical studies of Antarctic and Arctic rocks, soil, and sediments [37, 38]. The element-specific information on the surrounding electronic states, phase transition, magnetic properties, and molecular symmetry of nanoparticles are discussed extensively in the review articles on Mössbauer spectroscopy [39–41]. Most of the applications on Mössbauer spectroscopy focus on the corrosion and phase identification of materials rather than quantification [39]. Many reviews also widely cover the use of this technique in studying mineralogical composition of Fe-containing rocks, dust particles, and meteorites [35, 42]. Moreover, recent reviews concentrate on the structural and electronics characteristics of iron centres in relation to the dynamics of biomolecules and the examination of catalytic mechanisms through the oxidation state and coordination of Fe centres [43–46]. It is implemented in the analysis of cation binding sites in metalloproteins, supramolecular structure and in microbial cells or tissues [47]. Mössbauer spectroscopy has been extensively used in the field of electrocatalyst for oxygen reduction reaction (ORR) to identify the chemical nature of the active site of complex such as Fe–N–C catalyst [33, 44]. Research has been extended in the field of environmental catalyst and energy catalyst for phase identification of the catalyst using Mössbauer technique [44]. Also people have focus on the review of high magnetic properties at low temperature and spin states in the solid-state interaction with gaseous O₂/H₂O mixture of central iron atom complexes [48]. In this perspective, the present reviews attempt to capture specific areas of research using Mössbauer spectroscopy in the hopes of inspiring and encouraging the scientific community to pursue new insights in this research methods. In the published review articles, the information about the iron IONPs, spin dynamics, and structural transformation were not reported in detail.

From the above discussion, it is well visible that the potential applications of IONPs are strongly dependent on their intrinsic properties (i.e. shape, size, surface area, stoichiometry, etc.) and nature of the material. Therefore, the properties of iron oxides will feature differently for bare IONPs, iron oxide nanocomposites (IONCs) (with or without core–shell formation) or organically modified capped IONPs depending on the preparation routes. This brief review is focused on the effect of structural transformation and addition of other materials on the functionalization of Fe-based oxides studied using Mössbauer spectroscopy. It reports on the changes observed in the local environment of Fe atom with no interference from the other elements. Moreover, this work tries to address some existing uncertainties in the phase transition and spin dynamics of iron-based oxides in core–shell and capped nanostructures, including the self-diffusion dynamics of Fe-containing nanoparticles. Besides, the self-diffusion dynamics of Fe-containing nanoparticles in liquid media was also discussed to highlight the importance of looking into selected approach of the technique. Instead of serving as the main focus of research, this spectroscopic approach is well established and serves as a tool for chemical–physical characterization. So, the adaptability, originality, and high informational content of the method can be improved through construction of adequate model for selective research.

**Commonly studied polymorph of iron oxides and hydroxides**

Iron oxides (iron and oxygen chemically bonded) consist of the approximately 16 known polymorphs [6]. Among them, the three most common polymorph of iron oxide found in nature are magnetite (Fe₃O₄), hematite (α-Fe₂O₃), and maghemite (γ-Fe₂O₃) Fig. 1.
Magnetite (Fe₃O₄)

Magnetite (a polymorph of IONPs) has a cubic spinel structure with space group of Fd₃m where 32 O²⁻ ions form an fcc closed packing along the [111] plane and Fe atoms occupy the interstitial positions (Fe cations occupying tetrahedral Fe³⁺ and octahedral Fe²⁺,Fe³⁺ sites) [7]. Magnetite (Fe₃O₄, containing Fe₈ and Fe₀ in the 1:2 stoichiometric ratio) crystallizes in the inverse cubic spinel structure Fd₃m above the so-called Verwey transition temperature ~ 120 K [49]. Fe₃O₄ nanoparticles exhibit unique and tunable fundamental size- and shape-dependent novel magnetic, optical, and other unique properties due to quantum confinement effect, i.e., the nanometer size effect and have attracted great attention in recent years [49]. Fe₃O₄ nanoparticles (below 10–13 nm in size) often exhibit superparamagnetic characteristics. Neel relaxation of superparamagnetic Fe₃O₄ is found to be effective in the application of therapeutic hyperthermia and theranostic technologies through heating up the nanoparticles and the surrounding tissue by transferring energy from the external magnetic field. They exhibit ferromagnetic ordering.

Hematite (α-Fe₂O₃)

Hematite is one of the most stable polymorphs of IONPs under ambient conditions. They are widely used in the application of catalysts, adsorption, pigments, gas sensors, etc., due to its low cost and high corrosion resistivity [29]. Hematite crystallizes in the most common structure rhombohedral lattice system with space group of R3C and unit cell having lattice constants of a = 5.03 Å and c = 13.75 Å. The structure form a sixfold symmetry with O ions stacked along the [001] directions and the FeO₆ octahedra share edges inside the basal (001) plane. As similar to magnetite, hematite also shows superparamagnetic relaxation in ultra-fine (< 10 nm) structure. At low temperature below 260 K, they exhibit antiferromagnetic ordering. However, at temperature between so-called Morin temperature (~ 260 K) and Neel temperature (~ 970 K), reorientation of spin takes place and is slightly canted destabilizing the antiparallel spin and developing weak ferromagnetic behaviour [29]. Above the Neel temperature, they behave as paramagnet. However, it is to be noted that the magnetic properties are dependent or various factors viz., size, pressure, temperature, defects, surface phenomena, etc.

Iron hydroxide and oxyhydroxides (FeOOH)

Iron hydroxides and oxyhydroxides are also widely studied phase of iron-based compounds. Out of which Goethite (α-FeOOH), akaganeite (β-FeOOH), (γ-FeOOH) are commonly discussed. α-FeOOH exhibits are orthorhombic symmetry with a space group Pnma. It has a lattice parameters a = 9.95 Å, b = 3.01 Å, c = 4.62 Å [50]. Goethite has various range of shapes of which most commonly observed shape is acicular. Its building block comprises FeO₆(OH)₃ octahedra that forms a significant tunnel-like shape and stretch out in the direction of (010) plane, where hydrogen atoms are situated. Through its four edges and three vertices, each octahedron in α-FeOOH is connected to eight other nearby octahedral, while the oxygen atoms are in tetrahedral geometry [50]. In the case of iron oxyhydroxide phase (β-FeOOH), iron atoms are tightly bound to the framework which features a huge tunnel-type structure. Besides, Lepidocrocite, γ-FeO(OH), is a mineral that has a crystal structure made up of two layers of Fe octahedra, with hydroxyl groups on their exterior surfaces that form hydrogen bonds between the layers. These hydroxyl group forms a continuous O–H–O–H–O–O chains with symmetric hydrogen bonds. The iron hydroxides are generally antiferromagnetic in nature. Therefore, coexistence with cubic iron oxides may result to interesting magnetic

Figure 1: Schematic crystal structure of hematite, magnetite and maghemite.
phenomena such as exchange bias interaction, and the composites may have interesting catalytic properties.

**Maghemite (γ-Fe_{2}O_{3})**

Maghemite is an inverse spinel structure with a cation deficiency where Fe^{3+} is distributed on to the tetrahedral and octahedral sites. It crystallizes in cubic lattice system with lattice constant \( a = 8.33 \text{ Å} \). 64/3 of Fe^{3+} ions per unit cell are distributed among 8 tetrahedral and 16 octahedral sites and 8/3 of sites per unit cell are vacant [51]. The vacancy thus leads to different arrangement of the crystal giving rise to tetragonal symmetry (with space group P4_{3}2_{1}2) or partially ordered cubic crystal (with space group P4_{3}3_{2}1). Maghemite are widely used in the applications of anticorrosion paints, magnetic pigments in recording and storage media, catalysis, gas sensors and also in biomedical application [51]. They exhibit ferrimagnetic ordering.

**Working principle of Mössbauer spectroscopy**

In the field of solid-state research, Mössbauer spectroscopy has evolved into a beautiful and adaptable analytical tool. It can provide an immediate response to the valence state (oxidation state, spin state), local symmetry, or magnetic characteristics of a Mössbauer atom present in the material of interest in routine analyses [52]. Additionally, even when a material does not naturally have a Mössbauer-active nuclide as a constituent, it can still be doped with trace amount of Mössbauer-active element, which has proven beneficial in investigating different sorts of phase transitions.

The Mössbauer effect is the emission and absorption of \( \gamma \)-rays as a result of recoilless nuclear resonance phenomena in the source and sample, respectively [52, 53]. A source nucleus in an excited state of energy \( E \) undergoes transition to ground state of energy \( E_0 \) by emitting a \( \gamma \)-ray of energy \( E_\gamma = E - E_0 \). The transition to the excited state of energy \( E \) in the nuclei of the sample occurs when the \( \gamma \)-ray is absorbed by a nucleus of the same kind (identical \( Z \) and \( N \)). To scan the hyperfine splitting in the nuclear energy level, the energy of the \( \gamma \)-ray from the source is needed to have a doppler shift. Therefore, a vibration at the source is required. The acquisition of Mössbauer spectra is accomplished through \( \gamma \)-ray intensity measurement in conjunction with precise radioactive source motion control. Thus, the radioactive source velocity and the intensity of the detected \( \gamma \)-ray gives the Mössbauer spectrum. The schematic diagram of the Mössbauer spectrometer is shown in Fig. 2. It consists of three main components: (a) detector unit, (b) velocity driving system, and (c) data accumulation unit [53]. The detector and the multichannel amplitude analyzer built on top of the high-speed digital oscilloscope make up the \( \gamma \)-ray detection component. However, the velocity signal generator, feedback control system (proportional-integral-derivative, or PID), and electromechanical linear transducer make up the Mössbauer spectrometer’s driving system. Data accumulation device gives combine information on the velocity of the radioactive source with the intensity of \( \gamma \)-rays.

The structure of the spectra obtained from \( ^{57} \text{Fe} \) Mössbauer spectroscopy were discussed in the review article by Ernö et al. [41, 48]. The radioactive source is generally embedded in the non-magnetic cubic material with high Debye temperature. This is to prevent the source element from internal Zeeman’s and Stark effect. The \( ^{57} \text{Fe} \) in the sample experiences similar environment to that of the source; the spectrum obtained will be a singlet with isomer shift at 0 mm/s. The environment of the \( ^{57} \text{Fe} \) in the sample differs from that of the source or the difference in the oxidation state, then there will be a shift in the isomer shift from 0 mm/s. Then comes the local structure around the \( ^{57} \text{Fe} \) atoms. If the crystal structure exhibits a symmetric system then the spectrum will be a singlet. On the other hand, for the asymmetric system, the spectrum will convert to a doublet. If the system is magnetic (i.e., ferro, ferri or antiferromagnetic), the spectrum will have a resolve sextet. The structure of the spectrum discussed above is for a large size particles. For investigating an IONPs, the surface spin disordering on the surface will result in the increase in the width of the sextet. Further decreasing in the size below the superparamagnetic regime, the sextet will transform to a doublet.

**Discussion**

**Nucleation of nanoparticles**

The nanoparticles synthesized from various methods were characterized and found to have potential applications in modern technology [7, 54]. To obtain the desired nanoparticles of certain size and shape, optimization of the synthesis parameters are in the priority. Synthesis of nanoparticles using aqueous solution often results in large particles. Therefore, various additional
agents were introduced to tailor the physical, optical, and magnetic properties of the nanoparticles. Particle size was controlled by varying the polarity of the solution by addition of non-polar solvent [55]. Nucleation of nanoparticles can also be altered by addition of cationic deficient particles such as zeolite during the synthesis [56]. The particle size were found to be decreasing when the content of zeolite were increased. It is also observed that the particle size of the IONPs decreases as the incubation time of the zeolite in the iron precursor’s solution increases. The thermal stability of the iron oxide nanoparticles grown on the zeolite got enhanced by more than 100 K as compared with the bare IONPs. Addition of reducing agent is also found to tune the stoichiometric and morphology of the nanoparticles [57]. Using sodium acetate as the reducing agent for synthesizing IONPs through hydrothermal mode of synthesis plays a very important role on the morphology which reflected to magnetism. Apart from understanding the growth, structural, electrical and magnetic properties, the physics behind the interaction of the nanoparticles with the capping agents, drugs to be delivered and toxic compounds from the environment must also be addressed in order to optimize for biomedical and environmental applications [6, 57]. The size effect and the surface interaction with external agents affecting the spin dynamics of the $^{57}$Fe nuclides in SPIONs can be efficiently investigated using Mössbauer spectroscopy.

**Mössbauer studies on bare IONPs**

$^{57}$Fe Mössbauer spectroscopy is one of the effective methods to study the local structure of IONPs [29]. It is a non-destructive technique for phase identification of both IONPs and superior than X-ray diffraction in this regard. $^{57}$Fe Mössbauer spectroscopy is very sensitive to the local environment of the Fe atom. The hyperfine parameter extracted from the Mössbauer spectra, isomer shift ($\delta$), quadruple splitting ($\Delta$), and hyperfine field ($B$) provides information about the magnetic ordering, electron density, and its symmetry of the probe nucleus. Other parameters such as spectral width, relative intensities with asymmetries, and temperature dependence of hyperfine parameter can also provide valuable information on valence state, level of ordering, and stoichiometry of the IONPs and its composites [29]. Some of the Mössbauer hyperfine parameters of IONPs are highlighted in Table 1 which will be discussed later on.

Mössbauer studies were carried out to a large extent and were well documented [11, 29, 62]. It is utilized effectively to determine the cationic distribution. The magnetite ($\text{Fe}_3\text{O}_4$), a strong candidate of inverse spinel ferrites, exhibits mixed ferrites as the particle size decreases [31]. The isomer shift of the $^{57}$Fe at tetrahedral site of the as-synthesized nanoparticles decreases to 0.26 mm/s from 0.36 mm/s as the nanoparticles got annealed at 973 K in $10^{-3}$ mbar. On the other hand, the isomer shift ($\delta$) of $^{57}$Fe at octahedral site increases from 0.37 to 0.66 mm/s. These indicate the Fe$^{3+}$ and Fe$^{3+}$ coexist in the tetrahedral and octahedral sites in the as-synthesized nanoparticles. As the annealing temperature increases, the particles size increases and the decrease in the isomer shift at tetrahedral sites indicates the migration of Fe$^{3+}$ to the octahedral sites. Similarly, the Fe$^{3+}$ from octahedral migrates to tetrahedral which got reflected in the isomer shift. Mössbauer spectroscopy is often employed to determine the cationic distribution in doped iron oxides such as $\text{Zn}_{x}\text{Co}_{1-x}\text{Fe}_2\text{O}_4$, $\text{Mg}_{x}\text{Fe}_{3-x}\text{O}_4$, and $\text{Co}_{x}\text{Fe}_{3-x}\text{O}_4$ [63–65]. During the synthesis and even in the dispersed colloidal solution, the IONPs’ interparticle magnetic interactions frequently cause the particles to agglomerate and settle [66]. The magnetic interaction among the nanoparticles with respect to time were investigated using Mössbauer spectroscopy. The interaction among the SPIONs when preserved at ambient temperature in a vacuum desiccator for 31 months is reflected in the width of the superparamagnetic doublet [67]. The width was found to be increased by 0.15 mm/s, whereas the iron oxide nucleated in zeolite template was increased by 0.04 mm/s. This is proposed due to the enhanced magnetic interaction as a result of dehydration which decreases the interparticle distance with the course of time. On the other hand, the superparamagnetic doublet nucleated on zeolite powders shows almost similar width even after 31 months. Joos et al. have reported the oxidation of the bare magnetite which completely transformed to maghemite when the sample were aged for 21 months [68]. The increase in the magnetic hyperfine field after ageing were also observed. This may be due to the increase in the interparticle magnetic interactions. The coexistence of iron-based compounds along with iron oxides experiencing superparamagnetism cannot be identified using Mössbauer spectroscopy. Therefore, the inclusion of external magnetic field along with low temperature resolve the issue of superposition.

Coexistence of iron hydroxides in the form of amorphous or crystalline along with IONPs are often found when synthesized using co-precipitation [69–75]. The coexistence of hydroxides may increase the scope of application as iron hydroxides are utilized in environmental remediation such as prevention of accumulating the organic compound in paddy soils, toxic dye adsorption, etc. [76, 77]. However, the optimization of the magnetite is also important for specific application. Therefore, a prior treatment to the as-synthesized nanoparticles to ensure the reduction of hydroxides is essential if coexisted. The structural evolution of the coexisting iron hydroxides with magnetite is documented using Mössbauer spectroscopy [70–72].

The thermal effect on the variation of hyperfine parameters of the cubic iron oxide coexisting with iron hydroxide is shown in Fig. 3. The variations of hyperfine parameters are due to modifications in the local structure and magnetic properties at Fe sites as a result of desorption of –OH from α-FeOOH.
From the Mössbauer investigation on the thermal reduction of α-FeOOH, the temperature effect can be categorized into three zones. At low-temperature region of 300 K < T < 375 K, there is a decrease in the interparticle separation of α-FeOOH particles as a result of which dehydration of water molecules interdispersed between them. In the temperature regime of 400 K < T < 500 K, α-FeOOH transforms to maghemite (γ-Fe₂O₃). While in the higher annealing temperature interval from 500 K < T < 650 K, partial conversion of α-FeOOH to γ-Fe₂O₃ occurred and was further reduced to off stoichiometric magnetite. Annealing beyond 520 K predominantly results to the topotactic conversion of α-FeOOH to α-Fe₂O₃.

Interaction of the post-treated optimized or singly phased cubic iron oxide with the external agent such as toxic organic dyes and particles in the solvent were carried out using Mössbauer spectroscopy. It provides more insights into the kinetics of the interaction between the alkali ions and the IONPs in the solution. Mössbauer studies were carried out on the bare cubic IONPs incubated in the alkali solutions. The mean hyperfine field of the IONPs incubated in alkali solutions (LiCl (aq), NaCl (aq) and KCl (aq)) were found to be higher than that of the bare IONPs (Fig. 4). On the other hand, the mean hyperfine field of the IONPs incubated in alkali hydroxide solutions is lower than the bare IONPs. The increase in the mean hyperfine field proposed is due to the increase in the dipole–dipole interaction caused by the adsorbed alkali ions. However, the reduction in the $\langle B_{hf}\rangle$ in alkali hydroxide-incubated IONPs is due to the migration of

### TABLE 1: Hyperfine parameters of RT Mossbauer spectra of some of the IONPs with core–shell, capped and IONCs.

| Component | Isomer shift (mm/s) | Quadrupole splitting (mm/s) | Hyperfine field (T) | RA | Phase | Synthesis method | Size (nm) | References |
|-----------|---------------------|-----------------------------|---------------------|----|-------|-----------------|---------|------------|
| Fe₃O₄     | 0.37 (1)            | 54.9 (1)                    | A                   | Microemulsion | 6.3 ± 0.9 | [58] |
|           | 0.32 (0)            | 4.23 (0)                    | A                   | Co-precipitation | 12.9 ± 3.7 | [59] |
| IGEPAL capped Fe₃O₄ | 0.38 (1)            | 54.7 (1)                    | A                   | 6.3 ± 0.8 |
|          | 0.32 (1)            | 4.66 (2)                    | A                   | 13.5 ± 4.5 |
| Phosphate capped Fe₃O₄ | 0.31 (1)            | 44.7 (3)                    | A                   | 13.4 ± 4.5 |
| Core–shell Fe₃O₄/γ-Fe₂O₃ | 0.32 (0)            | 0.00 (0)                    | A                   | 8.0 ± 3.0 | [60] |
| Core–shell Fe₃O₄/γ-Fe₂O₃ 33 °C | 0.32 (0)            | 0.038 (0)                  | A                   | 14.2 ± 1.7 |
| Core–shell Fe₃O₄/γ-Fe₂O₃ 90 °C | 0.32 (0)            | 0.038 (0)                  | A                   | 14.2 ± 1.7 |
| FeO/Fe₃O₄ | 1.37                | 0.649                       | A                   | 20 ± 2 | [61] |
| A—Tetrahedral; B—Octahedral; B1—Oct (Fe³⁺); B2—Oct (Fe²⁺); SPM—Superparamagnetic.
alkali in the lattice of IONPs which stabilizes the lattice and prevents stacking fault formation.

**Mössbauer studies on capped IONPs**

Capping on iron oxide nanoparticles (IONPs) can give us enhanced properties in the combined system with multi-functionality. As iron oxide oxidises readily under ambient condition, IONPs capped with various organic or inorganic capping materials provide enhanced saturation magnetization, biocompatibility, surface modification properties, protective coating thus offering better functionalization [79]. A protective capping layer will prevent direct contact and interparticle exchange interactions. It increases the interparticle distance on the surface of IONPs which reduces or eliminates the magnetic dipole interactions [79]. Reduction in magnetic dipole interaction will directly affect the magnetic properties such as magnetic anisotropy and blocking temperature which will greatly affect the properties of the nanomaterials [58, 79]. Darbandi et al. prepared IONPs capped with organic surfactant IGEPAL by using microemulsion technique as shown in Fig. 5(a) [58]. They have taken the Mössbauer spectra at low temperature...
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(4.2 K) in order to block the superparamagnetic behaviour. It is being reported that at high temperature, IONPs usually show superparamagnetic behaviour due to thermal excitation of magnetic relaxation. The superparamagnetic blocking temperature is defined by the temperature at which the magnetic relaxation time equals the nuclear Larmor precession time ~ 10⁻⁸ s. Mössbauer spectra taken by Darbandi and co. at low temperature of 4.2 K at a field of 5 T for bare IONPs and capped IONPs were fitted with three sextets. Two of the sextets correspond to tetrahedral and octahedral sites of Fe³⁺ species and the other corresponds to the octahedral sites of Fe²⁺ species. The hyperfine parameters of the third sextet for Fe²⁺ species was examined by them in order to understand the effect of surface oxidation and site occupancy in the case of capped IONPs compared to bare. It was found that the Fe²⁺ content on bare IONPs was 4% less compared to the capped IONPs. This was explained as due to the reduction in oxidation of Fe³⁺ on the surface of the IONPs as a result of organic capping [58]. It is also reported that the canting effects for capped IONPs were minimal and it does not affect the surface structure or the type of magnetic ordering [58]. It is concluded that organic capping can tailor the interparticle distance since the spin canting is not affected by it. Moreover, the average interparticle distance can be correlated with the magnetic properties such as effective magnetic anisotropy and blocking temperature as discussed earlier. Muthukumaran et al. also study the effect of capping agent phosphate and oleic acid on magnetite IONPs using Mössbauer technique [59]. They found the reduction in the mean hyperfine field of the capped IONPs as compared to bare magnetite and the hyperfine field was of the order magnetite > oleic acid capped magnetite > phosphate capped magnetite. The lower hyperfine field of phosphate capped magnetite was correlated with the higher shell thickness compared to oleic acid capped magnetite nanoparticles. Thus, the dipole interaction energy is least in phosphate capped magnetite. Additionally, they found the quadrupole splitting of all the samples to be in the range of 0–0.04 mm/s which suggests that local structure of the samples is not affected by the capping [59]. It is reported that the Fe²⁺ content in bare magnetite was 25% less compared to the oleic acid capped and phosphate capped IONPs [59]. Oxidation of Fe³⁺ is responsible for this events as discussed earlier. Thus, capping of IONPs can provide multifunctionality without affecting the local environment of the IONPs. The capping of iron oxide nanoparticles reduces the dipole–dipole interaction; however, the interaction of the capping agent or carbon composites with the surface atoms seems to modify the surface spin orientation. The width of the doublet and the coexisting sextet, if any, decreases. It is also found that the hyperfine field also increases along with an improved relative transmission resulting in a better spectra [70, 80].

Mössbauer studies on core–shell structures with IONPs

Progress in the technique for manufacturing new magnetic material has led to the emergence of new magnetic nanoparticles constituting of two or more properties, i.e., the core–shell nanomaterials. Such material produces a synergistic effect due to the interaction between the core and the shell. Core–shell IONPs are one of the most promising materials in various applications [81, 82]. In core–shell IONPs, changes in the composition and magnetic domain size can greatly affect its properties [83]. So, in order to understand these changes, we have to discuss the
Mössbauer spectroscopy technique of such core–shell IONPs, Fe₂O₃/γ-Fe₂O₃ (a combination of magnetite and maghemite) is one of the promising core–shell IONPs specially in biomedical applications as shown in Fig. 5(b) [60]. Kamzin et al. had developed a core–shell Fe₃O₄/γ-Fe₂O₃ structure for which they studied the Mössbauer spectra to understand the magnetic properties, nature of exchange shift and other effects constituting it [60]. They proposed a model where two sextets each being associated with the magnetite phase and maghemite phase in the Mössbauer spectra of core–shell Fe₃O₄/γ-Fe₂O₃ at 300 K. Besides, below Verwey transitions (Tᵥ = 119 K), they proposed a superposition of three sextets for magnetite at 80 K as the electron exchange cease at this point [60]. So, a total of 5 sextets (3 for magnetite and 2 for maghemite) for Mössbauer spectra of Fe₃O₄/γ-Fe₂O₃ at 80 K were suggested. However, the proposed model did not fit well with the experimental data and six sextets were needed to perfectly fit it. The component of the Mössbauer parameters depicts that the hyperfine field B of Fe₃O₄/γ-Fe₂O₃ were found to be weaker than their bulk counterparts. They claim that these results are due to the reduction in size of the core–shell IONPs [60]. The isomer shift value for tetrahedral magnetite were found to be corroborated well with the Fe³⁺ ions, but the isomer shift for octahedral environment was found to be significantly higher and it falls between the values of Fe³⁺ and Fe⁵⁺. This event clarifies due to the effect of electron hopping [60]. The additional sextet fitted at 80 K is explained as the product of iron ions at the surface layer of the maghemite shell which has a deficit of one half of the neighbours. The hyperfine field at the interface is also reduced and the formation of cantent spin structure at the interface is highlighted. It is concluded that the intermediate layer between core (Fe₃O₄) and the shell (γ-Fe₂O₃) has a possibility to be in a spin glass state [60]. Moreover, upon the increase of synthesis time, the thickness of the maghemite shell were found to increase. In another study, the core–shell Fe₃O₄/γ-Fe₂O₃ with particle size of 6–13 nm were successfully synthesized at varying temperature in the range of 33–90 °C by Ilyengar et al. [49]. Depending on the small size, they found a weak doublet which confirms the presence of small fraction of particles lying below critical size of superparamagnetic relaxation and two sextets confirming the magnetic ordering. The hyperfine parameters of the sextets indicate the formation of magnetite phase. Here also the hyperfine field (B) is found to decrease as the temperature increases which they described is due to drop in the magnetic moment due to the concentration of Fe³⁺ ion in larger particles (particles size were larger for higher temperature samples). They suggested that the isomer shift value of the core–shell Fe₃O₄/γ-Fe₂O₃ were affected by the temperature (i.e. the s electron density at the active nuclear site is affected) and the isomer shift value of Fe³⁺ ion in tetrahedral site is higher than the bulk magnetite [49]. They proposed that the segregative oxygination of Fe²⁺ ions at the surface caused it to diffuse out of the inner oxide core of the magnetite onto the surface, where it then acquired the Fe⁵⁺ state [49]. These events give rise to surface Fe⁵⁺ cations as well as cation vacancies. This was explained from the variation in the stoichiometric ratio to 0.80–0.85 instead of 0.5 for Fe at tetrahedral and octahedral site [49]. In the course of this process, the outer oxide layer thickens as maghemite group upon the surface providing a core–shell structure.

Kamzin et al. synthesized a magnetic core–shell FeO/Fe₃O₄ nanoparticles through thermal decomposition method [61]. The average particle size from the TEM (Transmission Electron Microscope) analysis were reported to be of 20 nm. The Mössbauer parameter measured at 296 K without any external fields revealed the presence of complex magnetic phases and a superparamagnetic behaviour typical of small particle size. The fitted Mössbauer spectrum was reported to present a doublet and four Zeeman sextets of IONPs in the magnetically ordered state. The weak paramagnetic doublet corresponds to the FeO (wustite) phase. Out of the four sextets reported two sextets comprise magnetite phase for Fe³⁺ in tetrahedral site and Fe⁵⁺ in octahedral site. The other two correspond to the γ-Fe₂O₃ and iron ions located in interfacial regions and in the surface layer of the nanoparticles. The value of effective hyperfine field (B) for core–shell FeO/Fe₃O₄ was found to be significantly lower compared to the magnetite macrystals. They suggested that this effect of weak hyperfine field is associated with the characteristics of small particle size [61]. One interesting fact about their study is that they have highlighted the possibility of containing superparamagnetic regime of magnetite, Fe₂O₄ inclusions with non-stoichiometric composition and interfacial states manifesting relaxation effects in the broad complex spectrum [61]. However, in the case of FeO/Fe₂O₃ nanoparticles that they prepared, the contributions of the said factors are negligible and the Mössbauer effect of these states may be weak and indistinguishable. Thus, they also proposed the possibility of interfacial Fe₂O₃/Fe₃O₄/γ-Fe₂O₃ structures although they treated γ-Fe₂O₃ composition to be of small contamination in Fe₂O₃ structure in their study and ultimately come to conclusion of manufacturing core–shell FeO/Fe₂O₃.

Further, Mukhtar et al. had prepared IONPs by the reduction of iron(III) chloride solution by the addition of sodium borohydride solution at different time variation of 0–6 h [84]. The IONPs were found to be in the form of chain Fe core oxide shell structure which was confirmed by FESEM and TEM analysis [84]. Mössbauer analysis was performed at 320 K to understand the changes in the magnetic ordering and phase identification of the core–shell IONPs prepared at 0 and 6 h. The best fit for Mössbauer spectra experimental data were acquired by one doublet and four sextets. They have reported a doublet with isomer shifts of 0.24 mm/s and quadrupole splitting of 0.94 mm/s in IONPs-0 h, and in IONPs-6 h with isomer shift of 0.21 mm/s.
and quadrupole splitting of 1.11 mm/s attributed to superparamagnetic nature of Fe\(^{3+}\) state. The four sextets specified the magnetic hyperfine ordering. It is reported that one of the sextets in IONPs − 0 h corresponds to the magnetite phase which was confirmed from the hyperfine parameters. So, small fraction of the magnetite was found to emerge as contamination to the pure hematite (α-Fe\(_2\)O\(_3\)) shell in IONPs-0 h. Nevertheless, magnetite phase was not found in the IONPs-6 h sample, i.e., sample with longer reduction time [84]. The other sextets correspond to bcc Fe and hematite phase. So, the core–shell IONPs structure that Mukhtar et al. developed constitutes a core of bcc Fe and α-Fe\(_2\)O\(_3\) shell. They also found the same conclusion that increase in duration of synthesis time increases the shell thickness. The possible mechanism for the formation of such core–shell IONP structure was explained as the effect of oxidation; at initial time (0 h), the zero valent Fe core was covered by magnetite and hematite shell and as the oxidation time increases the magnetite was gradually converted to hematite [84].

Apart from the core shell of different polymorphs of iron oxide, core shell of iron oxides and gold, silver, SiO\(_2\), etc. were synthesized [81, 82, 85, 86]. Baskakov et al. [85] found the increase in the hyperfine field in the surface layer of magnetite for the core–shell Fe\(_3\)O\(_4\)/Au nanocomposites. This consequence is explained by the interaction of Au atoms with the dangling bonds of magnetite. The dipole interaction is dependent on the shell thickness, increase in shell thickness will reduce the interaction resulting in collapse of the sextet into a doublet. The shell also provide a preventive measure from oxidizing the core.

**Mössbauer study on IONCs**

Here, we discussed the Mössbauer spectra of some of the IONCs to extract valuable information on the local structure and magnetic ordering. People have studied Fe\(_3\)O\(_4\)/ZnO nanocomposite for quite a while [87, 88]. However, there are some dissimilarities in result of the Mössbauer spectra of ZnO/Fe\(_3\)O\(_4\) NC. It is known that the ionic distribution in Fe\(_3\)O\(_4)/ZnO NC can be regulated in accordance with the Zn/Fe stoichiometry [89]. Roychowdhury et al. prepared Fe\(_3\)O\(_4)/ZnO NC by dispersing Fe\(_3\)O\(_4\) and ZnO under intense sonication with varying Fe\(_3\)O\(_4\) wt. concentration [90]. Two sextets corresponding to magnetite phase were found and no other phase were reported in the Mössbauer spectra. The Mössbauer parameters of the prepared sample exhibit well-developed magnetic ordering. Superparamagnetic relaxation of fine particles were not detected in their prepared samples but the presence of cation vacancy was mentioned by them. The magnetization and hyperfine magnetic field intensity were found to decrease with Fe\(_3\)O\(_4)/ZnO NC compared to bare Fe\(_3\)O\(_4\) nanoparticles [90]. In similar case, Yesusa Collantes et al. synthesized Fe\(_3\)O\(_4)/ZnO NC through precipitation of ZnO onto surface of Fe\(_3\)O\(_4\) seeds [91]. However, they did not find magnetic hyperfine ordering and instead found a central doublet only. This indicates that the Fe\(_3\)O\(_4)/ZnO NC they prepared has superparamagnetic ordering in the Fe sites. Additionally, their study suggest the possibility of attaining ZnFe\(_2\)O\(_4\) phase at the interface of Fe\(_3\)O\(_4)/ZnO NC as the peak intensity and line width of the NC changes compared to peaks of bare Fe\(_3\)O\(_4\) [91]. Gordon et al. also prepared Zn/Fe oxide composite at varying weight ratio of Zn/Fe [87]. At lower concentration of Zn/Fe (1:9), broad magnetic sextet Mössbauer peaks are observed with hyperfine field of 45.5(±0.4) T at RT. At other higher ratio of Zn/Fe (3:7, 1:1, 8:2, 9:1), they found a superparamagnetic doublet only with a quadrupole splitting of 0.56–0.64 mm/s and they described the doublet to be of nanosize Fe\(_3\)O\(_4\). However, they also checked the Mössbauer spectra of pure ZnFe\(_2\)O\(_4\) for which quadrupole splitting was 0.42 mm/s so they proposed the possibility of small fraction of ZnFe\(_2\)O\(_4\) hidden in the smeared spectrum [87]. RT \(^{57}\)Fe Mössbauer analysis of our recent study in plasmatreated ZnO/α-Fe\(_3\)O\(_4\) nanocomposites with Zn/Fe ratio of (1:1) has shown the formation of paramagnetic doublet belonging to ZnFe\(_2\)O\(_4\) with quadrupole splitting of 0.41–0.53 mm/s and three magnetic sextets belonging to α-Fe\(_3\)O\(_4\) and Fe\(_3\)O\(_4\) [92]. The quadrupole splitting of ZnFe\(_2\)O\(_4\) was found to be higher in this study compared to ideal value of (0.32–0.39) mm/s which is due to the presence of defects. At low temperature (80 K), partial inversion state of ZnFe\(_2\)O\(_4\) was observed where fraction of Fe occupy the tetrahedral sites leading to shift of the Neel temperature to higher value. Also, the quadrupole splitting of the Fe\(_3\)O\(_4\) was found to be low thus there is reduction of Fe\(^{3+}\) to Fe\(^{2+}\) cation with the some fraction of α-Fe\(_3\)O\(_4\) transforming to Fe\(_3\)O\(_4\) [92]

Mössbauer spectroscopy also provides an evidence for the cationic migration when the materials are exposed at high temperature. In many of the dielectric devices, the composites were often sintered above 1000 K. As the materials got sintered at high temperature, the cationic migration among the composites may occur. The cationic redistribution will alter the properties which is needed to be addressed. Investigation on the composites of CoFe\(_2\)O\(_4\) and ZnO at various heat treatment depicts the migration of Zn from the ZnO to the lattice of CoFe\(_2\)O\(_4\) replacing Co [93]. This was concluded as the sextet corresponding to CoFe\(_2\)O\(_4\) collapses to a paramagnetic doublet representing ZnFe\(_2\)O\(_4\) at 973 K. No sextet was evolved apart from the paramagnetic doublet at 1273 K; however, the composites were ferromagnetic. This is plausible when the dislocated Co escaped from the lattice of CoFe\(_2\)O\(_4\) at 1273 K enters the lattice of ZnO forming ferromagnetic Zn\(_{0.9}\)Co\(_{0.1}\).O.

Further, \(^{57}\)Fe Mössbauer analysis on IONPs with graphene oxide and reduced graphene oxide could give us a better understanding on how the local environment and magnetic ordering change in the central atom Fe with the inclusion of graphene oxide and reduced graphene oxide. The spectra obtained from IONPs/GO and IONPs/rGO composites exhibit
magnetic ordering \[94\]. At RT, the spectral lines are broadened in both the cases due to overlapping of several components which constitutes to different non-equivalent states of Fe ions. Both of them constitute two sextets while there is one additional central doublet present in the IONPs/GO composite. This gives an idea that some fraction of the iron ions are in paramagnetic state which is due to the presence of small particles as a result of particle size distribution \[94\]. The hyperfine parameters of the IONPs/GO sample indicate the presence of only Fe$^{3+}$ state and Fe$^{2+}$ state was not found. The hyperfine field values of 48.3 and 52.0 T correspond to A sites and B sites of Fe$^{3+}$ which is very close to the values of maghemite $\gamma$-Fe$_2$O$_3$. The hyperfine parameters found from the IONPs/rGO (annealed at 773 and 1173 K) were also found to be similar. Moreover, the Fe$_A$/Fe$_B$ ratio calculated from these samples are found to be 1.6 and 1.7 which is very close to that bulk maghemite (1.67). So, $\gamma$-Fe$_2$O$_3$ phase emerges when IONPs makes composites with either GO or rGO which was detected from the RT $^{57}$Fe Mössbauer spectra \[94\]. Further, one more Mössbauer component (sextet) which has a lower value of hyperfine field was fitted for IONPs/rGO. This is explained as due to the charge transfer interaction between iron and graphene oxide at the interface \[94\]. In the case of IONPs/rGO (annealed at 773 and 1173 K), another additional hyperfine parameters were fitted which corresponds to the hematite (α-Fe$_2$O$_3$) phase. Lyubutin et al. explained that this formation is due to the $\gamma$-Fe$_2$O$_3$ NPs which are not shielded with graphene oxide \[94\]. Although, it contains Fe$^{3+}$ ions only, it can be concluded that IONPs/rGO composites contain mixture of hematite and maghemite phase.

Recently, CeO$_2$-IONPs nanocomposites were developed for application in various field. Mössbauer spectra of CeO$_2$-IONPs NC annealed at 773, 873, and 973 K were analysed by Lunacek et al. \[95\]. The nanocomposite annealed at 773 K contains two central doublets and a broad sextet. They observed that the contribution of the doublet decreases as the annealing temperature increases from 773–873–973 K. It is found that the central doublet consists of two sub-doublets for the samples annealed at 773 and 873 K, while it vanishes in the case of 973 K \[95\]. It is being reported that one of the central doublet emerges due to the fraction of small particles which is found to be superparamagnetic in nature. This finding was supported by TEM analysis \[95\]. Moreover, the other sub-doublet with small fraction of 3.2% is due to the Fe ions located inside the CeO$_2$ or due to the contribution of Fe oxide–Ce oxide at the interface. It is being reported that the magnetic components for sample annealed at 773 K presents fractions of α-Fe$_2$O$_3$, $\gamma$-Fe$_2$O$_3$, ε-Fe$_2$O$_3$, Fe$_3$O$_4$ and charge transfer at interface. They have noted that the emergence ε-Fe$_2$O$_3$ could not be detected by XRD unlike Mössbauer spectroscopy which is more sensitive and powerful \[95\]. However, as the annealed temperature increases to 873 K, it reduces to α-Fe$_2$O$_3$, ε-Fe$_2$O$_3$, Fe$_3$O$_4$ only and further at 973 K to only α-Fe$_2$O$_3$. This shows that Mössbauer spectroscopy can give us an in-depth analysis of the local structure around the central atom with the proper study of its hyperfine parameters.

A detailed study on the nucleation of magnetite on the zeolite and the magnetic interaction were investigated by Mössbauer spectroscopy \[32, 56, 67, 96, 97\]. The hyperfine field of the magnetite decreases and collapse to a doublet when zeolite were introduced in the course of nucleation as shown in Fig. 6. The

![Figure 6](https://example.com/figure6.png)

**Figure 6:** (a) Percentage of the superparamagnetic doublet of the IONPs at room temperature and 80 K. The superparamagnetic doublet increases rapidly at room temperature when the zeolite were introduced. The IONPs exhibits 100% doublet when the amount of zeolite was 200 mg. However, at 80 K the doublet decreases to 15% (approx). The reduction of doublet from 100 to 15% at 80 K is understood as due to the large magnetic interaction among the IONPs. (b) Schematics of the nucleation of IONPs. As the amount of zeolite increases, the nanoparticles were accommodated in the pores and therefore decreases the magnetic interaction among the IONPs particles. (Reproduced with permissions from Ref. \[56\], Copyright (2016) Elsevier).
Fe₃O₄ is very small compared to the theoretical monodomain iron oxide to silica-coated IONPs. The hyperfine field of the bare ordered phase (i.e. superparamagnetic) is increased from bare and two sextets of Fe associated with magnetite (48%). The non-magnetite (61%) against the superparamagnetic doublet (52%) and two magnetic sextets which belong to the material characteristics. In 1960, Singwi and Sjölander [101] proposed that a Mossbauer spectrum (k) can be described as a space–time Fourier transformation of a self-correlation function G(R, t), as a result, atomic excitations within the lifetime can be directly observed as a spectrum line broadening. Based on their theory, people have tried to explain the diffusion of material by observing Mössbauer spectrum line broadening through the concept of atomic jump model, although there were some decrease in the hyperfine field was due to the confined growth on the zeolite template. The confined nucleation is probably due to the columbic interaction of the cationic affinity sites and the surface exposure to the solution. Therefore, the increase in the incubation time of the zeolite in the iron precursor solution results in the formation of lower particle size as depicted by Mössbauer spectra. Zeolite provides a perfect template which stabilizes the IONPs. The IONPs nucleated on zeolite-13× initiates the evolution of sextet only after heat treatment above 823 K which is due to the agglomeration [67]. However, the bare nanoparticles agglomerates by 523 K.

A brief insight into spin dynamics of capping and core–shell formation

The relaxation dynamics of IONPs are different when capping and core–shell formation occurs. Often, there is sharp sextet observed for the capped IONPs or core–shell IONPs compared to broader distribution of bare IONPs. The hyperfine parameters of the capped and core–shell IONPs are slightly altered when compared to the bare or core IONPs, indicating the changes in the magnetic relaxation. N. Mahmad et al. [98] prepared iron oxide and silica-coated IONPs which form a core–shell formation. The bare IONPs was fitted with 8% superparamagnetic doublet, two independent sextet corresponding to magnetite (39%) and two distributed sextets which correspond to Fe associated with surface spin (53%). One of the distributed sextets has very low hyperfine field which indicates a weakened magnetic interaction at the surface. On the other hand, silica-coated iron oxide core shell has a distributed doublet (39%) which correspond to superparamagnetic state or isolated Fe cation dissolved in the silica shell, two independent sextets of magnetite (20%) and one distributed sextet of Fe related to the surface spin (41%). The fraction of Fe linked to surface disordered spin for silica-coated iron oxide core shell is less compared to the bare iron oxide and thus the hyperfine field of the Mössbauer parameter increases. In addition, Anne-Laure Morel et al. [99] also synthesized Fe₃O₄ and silica-coated Fe₃O₄ nanoparticles. The Mössbauer spectra of the bare Fe₃O₄ nanoparticles were fitted with one superparamagnetic doublet (39%) and two magnetic sextets which belong to the magnetite (61%) against the superparamagnetic doublet (52%) and two sextets of Fe associated with magnetite (48%). The non-ordered phase (i.e. superparamagnetic) is increased from bare iron oxide to silica-coated IONPs. The hyperfine field of the bare Fe₃O₄ is very small compared to the theoretical monodomain value of ~ 25 nm. This may be because of the small particle size distribution 4–10 nm of the prepared bare iron oxide particles. Moreover, Herojit et al. [70] also synthesized bare IONPs and oleic acid (OA) capped IONPs. Bare IONPs are fitted with 35% superparamagnetic doublet of Fe associated with α-FeOOH and Fe₂O₃ whose size is less than 10 nm, three sextets with 18% Fe of goethite, 3% Fe of γ-Fe₂O₃ and 45% Fe associated with surface disordered spins. The surface disordered spin is due to variation in the superexchange interaction of Fe–O–Fe which leads to random orientation of magnetic moment, thereby giving lesser hyperfine field. While OA capped IONPs was found to have similar hyperfine parameters, the fraction of Fe associated with the surface disordered spins is less (38%) compared to bare uncoated IONPs (45%). This concludes that capping has reduced the fluctuation of spins. The reduction in the orientation of the spins leads to slight increase in the hyperfine field of the OA capped IONPs which is clearly depicted in Table 2.

Capping or shell formation on the surface of the IONPs isolate the particles from agglomeration which leads to reduction in interparticle interaction. The interparticle interaction involves dipole–dipole interaction and exchange interaction through the surface of the IONPs [98, 100]. This dipole–dipole interaction is directly linked to the magnetic anisotropy energy barrier. Thus, decrease in the interparticle interaction reduces the effective magnetic anisotropy energy and vice versa. This affects the spin ordering at the surface of the IONPs particles which in turn affects the magnetization of the particle [98]. For bare IONPs, the particles are loosely bound to each other with dipole–dipole interaction and magnetic moment of each particle orient randomly from the isolated particles [98, 99]. The dipole–dipole interaction in bare IONPs enhances the magnetic anisotropy due to large number of free surface spin. The presence of magnetic phase in Mössbauer spectra is related to this interaction. However, in the case of capped or core–shell IONPs, the decrease in the interparticle interaction reduces dipole–dipole interaction which leads to improvement of the surface spin ordering [99, 100]. The reorientation of the magnetic moment on the surface of the IONPs may occur which is influenced by the magnetization from the capped or the shell formation (the degree of randomness decrease as shown in the schematics Fig. 7). Moreover, the electrostatic interactions of capped or shell polar molecules with IONPs which is related to ⁵⁷Fe magnetic hyperfine field is affected (decrease in Fe spin disorder when capped) [100]. Thus, a sharp line spectra and increased hyperfine field are followed for capped or core–shell IONPs.

Mössbauer spectroscopy for diffusion

Diffusion is an important phenomena to control and improve the material characteristics. In 1960, Singwi and Sjölander [101] proposed that a Mossbauer spectrum (k) can be described as a space–time Fourier transformation of a self-correlation function G(R, t), as a result, atomic excitations within the lifetime can be directly observed as a spectrum line broadening. Based on their theory, people have tried to explain the diffusion of material by observing Mössbauer spectrum line broadening through the concept of atomic jump model, although there were some...
discrepancies in earlier experimental research for the Mössbauer diffusivity deduced from the line broadening based on the said theory. The self-diffusion of pure Fe with the ultra-high vacuum furnace thermal treatment at high temperature gives the first positive result on the diffusion mechanics [102]. However, different precise experimental setup has to be considered for various diffusion mechanism. For example, diffusion mechanism into the interstitial site required the construction of an in-beam setup which incorporated coulomb excitation with a recoil implantation technique [103, 104]. Long-range interstitial diffusion of Fe in Si was observed at ~ 500 K through interpretation of line broadenings [105]. The line broadenings and relaxation of two corresponding components could be used to detect interstitial and substitutional $^{57}$Fe diffusion [106]. However, discussion or experiment carried out in the past were of homogeneous solids and also the diffusion length and time characteristics for the correlation functions were decided of few nanometers and 10$^{-6}$–10$^{-8}$ s, respectively [103–105, 107, 108]. Nevertheless, most of the materials that we study are heterogeneous (i.e. microstructures) in nature. These microstructure characteristics will greatly influence the diffusion mechanism in the material. For instance, crystal grains, lattice defects and dislocation are present in the materials and the diffusion is influenced by the internal stress field [109]. So, to control the microstructures, a

Table 2: Few examples of capped IONPs and core–shell IONPs and their Mössbauer parameters.

| Sample           | $\Gamma$ (mm/s) | $B$ (T) | RA | Phase                  | Nature    | Synthesis technique            | Size (nm) | References |
|------------------|-----------------|---------|----|------------------------|-----------|--------------------------------|-----------|------------|
| Fe$_3$O$_4$      |                 |         |    | SPM                    | Core      | Co-precipitation               | 15        | [98]       |
|                  | –               | 8       |    | Fe$_A$                 |           |                                 |           |            |
|                  | 47.4            | 21      |    | Fe$_A$                 |           |                                 |           |            |
|                  | 43.0            | 18      |    | Fe$_B$                 |           |                                 |           |            |
|                  | 36.0            | 34      |    | Surface                |           |                                 |           |            |
|                  | 19.0            | 19      |    | Surface                |           |                                 |           |            |
| Fe$_3$O$_4$@SiO$_2$ | –              | 39      |    | SPM/dissolved Fe ions in shell | Core–shell | Modified Stober method          | 145       |            |
|                  |                 |         |    | Fe$_A$                 |           |                                 |           |            |
|                  | 48.1            | 8       |    | Fe$_A$                 |           |                                 |           |            |
|                  | 45.1            | 12      |    | Fe$_B$                 |           |                                 |           |            |
|                  | 39.5            | 41      |    | Surface                |           |                                 |           |            |
| Fe$_3$O$_4$      | 0.30            | –       | 39 | SPM                    | Core      | Sonochemical method             | (4–10)    | [99]       |
|                  | 0.35            | 7       | 61 | Fe$_A$                 |           |                                 |           |            |
|                  | 0.50            | 13      |    | Fe$_B$                 |           |                                 |           |            |
| Fe$_3$O$_4$@SiO$_2$ | 0.40           | –       | 52 | SPM                    | Core–shell| Sonochemical method             | (5–11.5)  |            |
|                  | 0.50            | 34      | 48 | Fe$_A$                 |           |                                 |           |            |
|                  | 0.50            | 36      |    | Fe$_B$                 |           |                                 |           |            |
| IONPs            | 0.69            | –       | 34.9| SPM                    | bare      | Co-precipitation                | 6         | [70]       |
|                  | 5.10            | 22.3    | 44.9| Surface                |           |                                 |           |            |
|                  | 0.84            | 36.8    | 17.2| $\alpha$-FeOOH         |           |                                 |           |            |
|                  | 0.67            | 45.9    | 03.0| $\alpha$-Fe$_2$O$_3$   |           |                                 |           |            |
| OA coated IONPs  | 0.86            | –       | 35.8| SPM                    | OA capped | Co-precipitation                | 8         |            |
|                  | 3.73            | 23.9    | 38.3| Surface                |           |                                 |           |            |
|                  | 0.97            | 37.3    | 22.4| $\alpha$-FeOOH         |           |                                 |           |            |
|                  | 0.83            | 47.5    | 03.5| $\alpha$-Fe$_2$O$_3$   |           |                                 |           |            |

SPM—Superparamagnetic, Fe$_A$—tetrahedral site, Fe$_B$—octahedral site.

Figure 7: Schematics on the spin dynamics of superparamagnetic and magnetic IONPs with surface capping and core–shell formation.
new methodology must be developed. Also, diffusion studies in liquid media using Mössbauer technique are hardly found and have to be taken into account for a possible new insights.

A new technique called Mössbauer spectroscopic microscope (MSM) technique has been developed by Yoshida et al. to study the Fe diffusion on Si wafer [106]. These technique can measure the diffusion profile of Fe states in Si separately. Also this method allows researchers to investigate diffusion processes while accounting for interactions and correlations between Fe impurities and grain boundaries, lattice defects and dislocations in different grains. Recently, a new approach of Mössbauer spectroscopy technique had been established to quantify the nanoscale diffusion and hydrodynamic properties of iron-containing nanoparticles (NPs) in liquid media [110]. They are widely used in a variety of biomedical fields, including drug delivery, MRI and hyperthermia [111, 112].

The fact that Mössbauer spectroscopy is sensitive to only $^{57}$Fe nuclei distinguishes such measurements, as it allows for the determination of the NP self-diffusion coefficient in medium of any complexity, regardless of solution transparency, constituent concentration, or crowding agent type. As a result of the Doppler shift, the averaged parameters of NP diffusion motion are directly reflected in the features of the obtained Mössbauer spectra, removing the spatial limitation of the diffusion measurement. For instance, CoFe$_2$O$_4$ is dispersed in bovine serum albumin (BSA) and glycerol solution with a volume fraction of 0–0.2 [112]. It is being observed that the Mössbauer spectra are highly sensitive to the diffusion of CoFe$_2$O$_4$ nanoparticles in liquid media which is confirmed by the broadening of the spectra. When the volume fraction of bovine serum albumin is 0.2, the CoFe$_2$O$_4$ normalized diffusivity is reduced by 86% in comparison to 0 volume fraction of BSA [112].

The diffusion motion of CoFe$_2$O$_4$ NPs in liquid media can be depicted with a single strongly broadened line which constitutes the hyperfine parameters of a magnetic sextet usually observed in powder sample. The strong broadening observed in Fig. 8 is due to the diffusion phenomenon. The proposed technique is based on the idea that the Brownian motion of $^{57}$Fe containing in crowded solutions influence the γ-quanta absorption spectrum as well as the Doppler shift from γ-source movement.

The only difference between this experiment and the powder analogues is that diffusion in liquid media results in the appearance of a broad distribution of γ-ray velocity (energy), i.e., a broadening of the Mössbauer line. It is self-evident that diffusion properties can be reliably evaluated from Mössbauer spectra in a range limited by the natural line width as a lower boundary and the velocity range realized in experiments as an upper boundary. The relation between the broadening of line width $\Delta \Gamma$ and $D_{\text{Mössbauer}}$ (diffusion coefficient) can be expressed as [101]

$$\Delta \Gamma = \frac{2kT D_{\text{Mössbauer}}}{\hbar c},$$

where $E_0$ is the energy of the γ-quanta (14.41 keV for $^{57}$Fe), $c$ is the velocity of light, and $\hbar$ is the reduced Planck constant.

From the equation, it is observed that $\Delta \Gamma$ is directly proportional to $D_{\text{Mössbauer}}$ and therefore can be used to quantify the self-diffusion of a material in solid or liquid media. These mechanism has also been checked using various scaling theoretical model which determine $D$ (self-diffusion coefficient) as a function of particle size, macromolecule type and its radius of gyration and correlation length which in turn depends on the concentration of macromolecule. The observed diffusivity behaviour turns out to be consistent with that using Mössbauer spectroscopy. Therefore, the developed method appears to be a very promising method for studying the diffusion of iron-containing NPs in complex media with a diffusion coefficient.

**Summary**

The structural, magnetic, and the corresponding local structure were effectively investigated. Therefore, Mössbauer spectroscopy can be employed to study the kinetics of phase
transition, nucleation growth mechanism, magnetic interactions, and the binding state of the nanoparticles among the bare, capped, core shell and nucleated on a template, etc. The studies on the determination of the local structure of $^{57}$Fe and the related spin dynamic is a prior information to understand the kinetics of the interaction with the atomic, ionic, molecular or polymers in different experimental conditions. Determination of the local structure can predict the defect, oxidation state and the cationic distributions in the crystal. This is a necessary investigation and will bring an insight which will assist to mimic the complex interaction of the nanoparticles with the biological agents, magnetism etc. In the literature, the Mössbauer parameters such as hyperfine field, quadruple splitting and width have shown a significant variation before and after the capping with organic capping agents or composites [80]. This may be due to the reorientation of the surface spin reducing the degree of random orientation. The investigation onto the dynamics of the surface spin as a consequence of the capping agent or shell layer formation give us some insights into it; however, further examination is required to clearly understand the effect of multi-layer capping or shell thickness for the particles especially beyond the superparamagnetic regime. The Mössbauer spectroscopy is known as an efficient and special technique to investigate the samples containing Mössbauer-active elements. However, a trace amount of active element in the compound or composites may result to a scattered or low-quality data. In these cases, to achieve a good quality data, the researchers should utilize the Mössbauer-active isotope during the synthesis.

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Author contributions
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Data availability
Data sharing is not applicable to this article as no datasets were generated during the study.

Declarations
Conflict of interest The authors declare no conflict of interest.

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