Review Article

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Review of synthesis and applications of Iron oxide nanoparticles

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Abstract: Iron Nanoparticles also known as nanoparticles of iron oxide have been recognized in various sectors mainly because of their size and high surface area which is available for utilization. In this paper, we have givena brief review of the synthesis technique and have given a brief idea about its applications. Given the current interest in iron nanoparticles, this review is intended to provide information on the synthesis and applications of Iron Oxide Nanoparticles. We have given a brief idea about Physical methods, Chemical Methods, and BiologicalMethods for synthesis. They mainly include techniques like electron beam lithography, Co-precipitation, Sol-gel, Hydrothermal, Microemulsions, and microbial incubation for iron nanoparticles (NPs).

Key Words: Iron oxide, Nanoparticles, Surface area, Synthesis, Application

1] Introduction

Nanotechnology is a relatively young scientific discipline concerned with particles or materials with sizes ranging from 1 to 100 nm. Particles of this range can help in simple adsorption, absorption,and penetration owing to greater interaction between the molecules[1]. Iron oxide nanoparticles have gained a lot of interest in recent years because of their applicability in various fields[1]. They can be obtained using various techniques and methods like physical, chemical, or biological. Chemical interactions between iron and oxygenresult in the formation of iron oxides (compounds), of which 16 have been discovered. In nature, rust is an example of iron (III) oxide[2]. Owing to their small size (diameter ranges from 1 to 100 nm), the Iron oxide nanoparticles have unique and regulated features that differ from the ones seen on the macroscopic magnitude,allowing for novel uses[3].It is well understood that when particle size decreases, the ratio of surface atoms to heavy atoms grows considerably. Nanostructured materials have a wide range of physical, chemical, optical, mechanical, electrical, and magnetic qualities because surface atoms have less coordination than big atoms[4]. Oxide of Iron is a mineral compound that exists in polymorphic forms such as hematite (Fe_2O_3), magnetite (Fe_3O_4), and maghemite (Fe_2O_3). Metallic iron oxide nanoparticles have a greater catalytic impact because of the smaller size of the particles, sites that are more active, and a large surface area, which encourages more adsorption of gas during heat oxidation processes. Nanoparticles which are made from materials of ferromagnet and have sizes of 10nm-20 nm show a unique magnetism form recognized as super-paramagnetism. The materials exhibiting ferromagnetic properties., comprising elemental metals, alloys, oxides, and diverse chemicals, undergo magnetization through an externallyapplied magnetic field. This significant phenomenon occurs solely in nanoparticle systems[5]. Magnetic iron oxide(Fe_3O_4 and g-Fe_2O_3) because of their low toxic effects, superparamagnetic features like surface area and its volume ratio, and methodology for simple separation, nanoparticles (NPs) have sparked a lot of attention. They are very appealing for biomedical applications[6].

Nowadays, Iron oxide nanoparticles can be produced by various methods like Electron beam lithography, Coprecipitation, Sol-gel, Hydrothermal, Microemulsions, and Microbial incubation. The above methods can be classified as Physical methods, Chemical methods, and biological methods [12].

To synthesize Nanoparticles of Iron oxides, the following three techniques can be used:

1.Physical methods: They are sophisticated techniques that are hampered by the difficulty of controlling particle size at the nanoscale level.

2.Chemical methods: They are relatively straightforward, manageable, and more efficient, providing control over the sizes, content, and shape of Nanoparticles produced[7]. Iron oxides are also synthesized by co-precipitating Fe^{2+} and Fe^{3+} with a base[8]. The type of salt employed, the ratio of $Fe^{2+}/Fe^{3+,}$ the pH of the solvent, and the ionic strength also influence the size, shape, and composition of nanoparticles ofIron oxide which are synthesized chemically.

3.Biological methods: Microbes have the natural capacity for nanoparticle synthesis due to their enormousdiversity, and they might be viewed as prospective biofactories for nanoparticle synthesis[9]. Amongst these production techniques, chemical methods are the most commonly used methods because of their high yield and low cost of production. In general, magnetites are produced by adding a base to a 1:2 molar ratio aqueous mixture of Fe^{2+} and Fe^{3+} chloride, which results in a black color[10]. The reaction for precipitation of black iron oxide is given as follows

$$Fe^{2+} + 2Fe^{3+} + 8OH \rightarrow Fe_3O_4 + 4H_2O$$

In an environment that does not comprise oxygen, precipitation of Fe_3O_4 is likely between pH 9 and 14, maintaining a molar ratio of Fe^{3+}: Fe^{2+} (2:1). The oxidation of Fe_3O_4 can be as follows :

$$Fe_3O_4 + 0:25O_2 + 4:5H_2O \rightarrow 3Fe(OH)^{3+}$$

Depending on the environment, the chemical and physical features of NPs may change. Fe3O4 Nanoparticles are typically organic coating or inorganic coating to prevent oxidation and aggregation of iron NPs. It remains essential to produce magnetic nanoparticles in an environment devoid of oxygen, preferably with the presence ofnitrogen gas. The introduction of nitrogen gas serves to safeguard the nanoparticles against oxidation and reduces their size[11]..Each method stated previously has its pros and cons. Although physical approaches are easy to use, control over particle size is complex. The size of the particle can be somewhat in wet chemical processing regulated by modifying conditions. The chemical methods include Co-precipitation, Sol-gel, Hydrothermal, and Oxidation. The most efficient method for producing iron magnetic NPs is in the aqueous medium in all of these techniques. It has been proven that modifying the related parameters such as the ratio of Fe^{2+}/ Fe^{3+},[8] bases like (NaOH, NH4OH, and CH3NH2), and strength of ionic solutions (1. Tetramethylammonium ion: $N(CH_3)_4^+$, 2. Methylammonium ion: $CH_3NH_3^+$, 3. Ammonium ion: NH_4^+, 4. Sodium ion: Na^+, 5. Lithium ion: Li^+,6. Potassium ion: K^+) could customize the particle size and polydispersity of the NPs. Other parameters that determine the dimensions of nanoparticles[11] include a rise in the rate of mixing, variations in temperature, and intake of Nitrogen Gas, Agitation speed, pH, and Ratio of the reactant. The microbial method is economical, and reproducible giving a higher yield, but having longer reaction times[9].

Techniques for synthesis of Iron Oxide Nanoparticles:

1]2.1] Physical methods:

2.1.1]

Electron Beam Lithography: is a process that includes projecting a patterned beam of electrons onto a substrate that is coated with resin or a film and removing strategically exposed or disclosed resin[13]. The approach for the synthesis of Iron oxide nanoparticles using the lithographic technique focuses an electron beam to produce tiny-sized iron oxide nanoparticles which outweighs the established techniques such as photolithography[14]. This process has been widely utilized to produce rods that are magnetic and nano in size and nanoring which are from the narrow metallic layers with an organic resin that are spin-coated on themselves[15]. A focused beam of electrons is employed to generate intricate trends on a film made of metal, subsequently soaked inside a bath of solvent. This action causes the excess metal to riseand evaporate, yielding nanoparticles smaller than 50 nm. Previous experiments have utilized an anion- assisted

hydrothermal method to synthesize Fe_3O_4 nanoparticles[16] [15] crafted single-crystal -Fe_2O_3 nano rings, later converting them into Fe_3O_4 and -Fe_2O_3 via the oxidation and reduction procedure. While this method can produce microscopic particles, it is accompanied by negatives like the high cost ofproduction, a prolonged procedure, potential issues with the scanning of the electrons, and constraints inresolutions[17].

2.2]

Biological Methods:

Nanoparticles of Iron oxide are also synthesized by means like bacteria, fungi, extracts from plants, as well as protein-mediated procedures. Given figures depict the production of Iron oxide nanoparticles from plant extract and microbes. Because of various reasons, there is very little information on biological agents used for the formation of Iron oxide nanoparticle formation. Bacteria was preferred to make nanoparticles of Iron Oxide, which were established beyond the cells to synthesize iron-based magnetic nanoparticles like Greigite (Fe_3S_4) which also provided an iron source[18]. Natural occurrence took place because nanoparticles of Iron oxide need particular conditions of the environment such as to be constructed are pH, pO_2, pCO_2, redox potential, and temperature. The induced biological biomineralization term is employed to define the cultured synthesis of the nanoparticles or crystals of iron oxide fluid extracellularly. Biologically controlled biomineralization (BCM) transpires when the synthesis unfolds within the intracellular compartment of magnetotactic or sulphur-reducing bacteria. This processing is restricted to specific locations inside the cytoplasm or the walls of the cell. Because this location is completely secluded from the outside world, it has optimal geochemical conditions. This processinvolves multiple phases, includes an overabundance of ferrous ions by transit at the specified matrix-
produced side, which is followed by highly regulated nucleation that results their orientation, shape, and size guided in a highly orderly growth. As a result, BCM generates well-ordered crystalline particles[19]. In addition to microbes, plant extracts offer an alternative for synthesizing Nanoparticles or metal nanoparticles of Iron oxide using an approach of bottom to up[20]. Madubuonu[21] successfully synthesized nanoparticles of Iron oxide having asize below 50 nm utilizing the extracts from the plants *Psidium guavaja* and *Moringa oleifera*. The findings indicated that the nanoparticles of Iron oxide exhibit anti-bacterial activity and showed degradation using photocatalytic activity of that equivalent to methylene blue. *Moringa oleifera* leaf extract was utilized to produce rod-like Iron oxide nanoparticles, characterized by an average size of the particle of 15 nm and displayed super-paramagnetism. Similar to spherical nanoparticles of Iron oxide, rod-like shape, counterparts exhibited a notable anti-bacterial activity[22]. Neem extracts (*Azadirachta Indica)* were employed as well in facilitating the formation of nanoparticles of Iron oxide[23]. Beyond plants and bacteria, Ferritin a protein form from viruses has proved to be efficient in serving as a route in order to synthesize nanoparticles of Iron oxide[24].

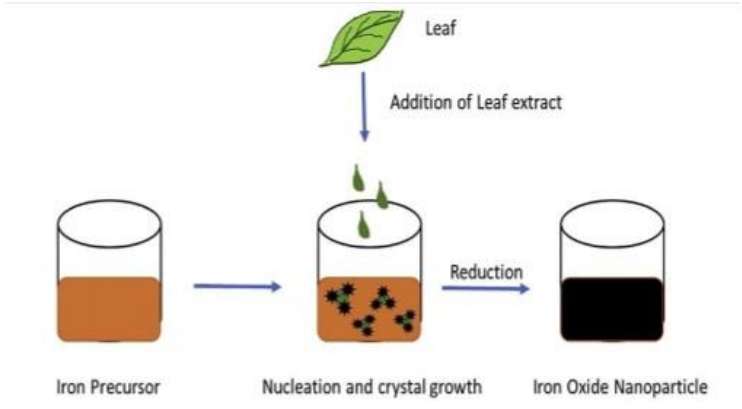

Fig 2.1: Iron oxide nanoparticles using plant extract

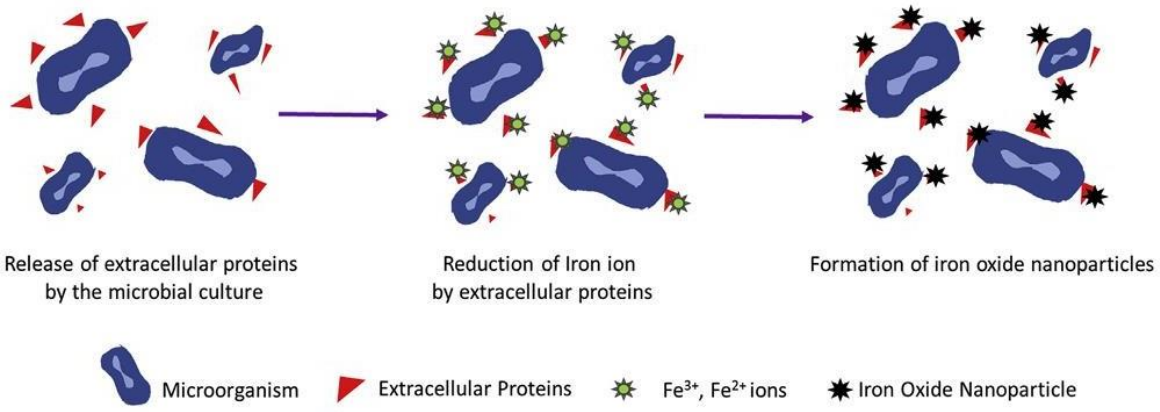

Fig 2.2: Iron oxide nanoparticles using microorganisms

2.3] Chemical Methods:

2.3.1]

Sol Gel Method: The Sol-Gel method relies on the hydroxylating and condensing molecular precursors ina liquid solution. The resulting sol occurring from nanometric substances is subsequently either dried or gelled to achieve three-dimensionality through solvent evaporation or the chemical reaction of a metal oxide network. Water serves as the employed solvent in this process. However, the precursors produced are hydrolysed with the use of acid or base. Acidic catalysis results in a colloidal gel, while alkaline catalytic activity generates a gel that is polymeric in nature[25]. This process is conducted at environmental temperature, although heat processing is necessary to attain the ultimate crystalline condition[26]. The acidity, composition, and amount of the salt predecessor, reaction speed, heat, stirring, and gel properties collectively influence the synthesis[27]. Magnetic ordering in this method is affected by solvent volume and phase, but it is also affected by Dispersion and dimension spread[28]. The pros include the ability to synthesize substances with a pre-established arrangement, entirely non-crystalline state, uniformity in size, precise management of particle dimensions, manipulation of microstructure, uniform product composition, and the capacity to produce integrated molecules that retain their stability and characteristics within the framework[6]. It is a simple process for producing metal oxides from salts under specified conditions. This method is also employed to create iron oxide–silica aerogel composites, which have been observed to exhibit greater reactivity compared to traditional Iron oxide. The process involves dissolving readily accessible precursors, specifically tetraethyl orthosilicate and Fe (III) solutions, in an aqueoussolution containing alcohol. The resulting gel is then subjected to heat to produce the final substances. The heightened reactivity is attributed to the extensive surface area of the iron oxide nanoparticles[29 28 30].

$$\text{Disproportionation: } Fe^{3+} + H_2O \rightarrow Fe(OH)_x^{3-x}$$

$$\text{Oxidation: } Fe(OH)_x^{3-x}$$

$$\text{Magnetite dehydration: } Fe_3O_4 \text{ (pH 9.0, 60°C)}$$

Fig 2.3: Reaction scheme

2.3.2]

Hydrothermal Methods: Originating from geological practices and first implemented by geoscientists in the 19th century in order to study particular rocks or mineral under induced hydrothermal conditions, the hydrothermal approach has

demonstrated its value in nanoparticle synthesis. This is attributed to its advantagesin producing finely-sized particles[31]. Hydrothermal responses take place in a reactor or autoclave submerged in a watery environment, upholding pressures surpassing the pressure of 2,000 psi and temperatures exceeding 200°C. The desiccation of salts of the metals and the limited solubility of oxides in the aqueous stage resulted inheightened supersaturation of the medium[32]. Hao and Teja did a thorough exploration, scrutinizing the influences of temperature, type of precursor, and duration on the structure and size of particles. Their observations reveal that elevated precursor concentrations lead to larger particles, with residence time exerting a more pronounced effect than concentration. Typically, particles with uniform distribution are generated during brief residence times[33]. The influence of modifying the concentration of the precursor, such as ferric nitrate, while keeping other factors constant, was investigated for various kind of experiments. Images obtained from Transmission electron microscopy (TEM) images of the particles revealed a rounded configuration with an average particle radius of 15.6±4.0 nm. In specific trials where precursor concentration was varied, a small amount of large rhombic particles which had an average size of 27.4±7.0 nm were also observed.Despite these variations, most particles maintained a rhombic shape, with only a few smaller spherical particles[6].The main con of this process is that it needs expensive reactors[34].

2.3.3]

Microemulsions: These are thermodynamically stable isotropic mixtures consisting of oil, water, and surfactants, and are formed by component mixing without the need for high shear conditions. This versatile category encompasses direct emulsions (oil in water), reversed emulsions (water in oil), and bi-continuous structures. The reverse microemulsion method, utilizing surfactants, has proven successful in synthesizing small- sized metal nanoparticles of uniform dimensions. Numerous research and experiments have focused on generating microemulsions containing iron oxide nanoparticles. In the synthesis of silica-coated iron oxide nanoparticles, a reverse microemulsion method utilizing non-ionic surfactants has been employed[35]. Lopez Perez et al. conducted a reverse microemulsion method in order to produce Iron oxide nanoparticles, forming dropletsof water in an organic solvent to have control over the size of the particle[36]. Similarly, Chin and Yaacob group[37]reported the production of iron oxide nanoparticles in the size range approximating to 5–10 nm using a microemulsion method involving the dissolution of Hexadecyl Trimetehyleammonium Bromide (HTAB) in n-octane, followed by the addition of 1-butanol (Fig. 3). However, a notable drawback of the microemulsion method is its limitation in mass production. Through a co-precipitation reaction, monodispersed and coated small Iron oxide nanoparticles (specifically maghemite) were produced using ferrous and ferric salts, in combination with organic bases such as cyclohexylamine and oleylamine. This synthesis took place within a water-in-oil one-pot microemulsion[38]. Another study by Kekalo et al. utilized the microemulsion method employing three different surfactants (cetyltrimethylammonium bromide [CTAB], octane, and n-butanol). This resulted in the formation of iron oxide nanoparticles characterized by a core size ranging from 8 to 16 nm and a shell measuring 2 to 3 nm[39]

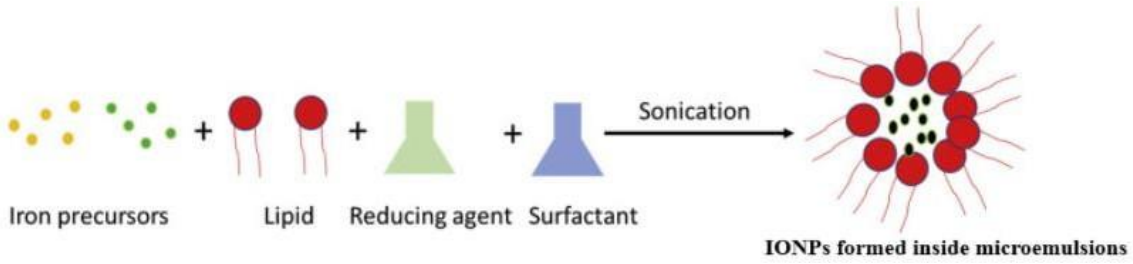

Fig 2.4: Encapsulation on Iron oxide nanoparticles

2.3.4] Co-precipitation: Precipitation from the aqueous solutions stands out as the most employed method. In this process the synthesis involves the reaction of Fe (II) salt in an aqueous solution with a base in the presence of a mild oxidant, resulting in the formation of spherical nanoparticles ranging from 30 to 100 nm[40]. The synthesisprocess is influenced by factors such as pH, nature and concentration of the salt precursor, kinetics, temperature, agitation, and gel characteristics[41]. Typically, agglomeration occurs due to the large surface area-to-volume ratioand is aimed at minimizing surface energy[42]. Dispersing agents like anionic surfactants are added to stabilize theIron oxide nanoparticles formed[43]. A weak reducing agent is used to reduce the precursors of iron to oxides of iron using agents like NaOH, NH_3, etc[40]. The pathway for the formation of Iron oxide nanoparticles from precursor molecules through spontaneous nucleation and growth can significantly differ. This variation is dependent on factors such as the pH strength of the reducing agents, the concentration of precursors, the nature of the reducing agents, and the rate at which the reducing agents are introduced. These alterations may lead to the creation of distinct Iron oxide nanoparticles, influenced by the specific design of each reaction pathway[44]. Proteins, starches,

nonionic detergents, or polyelectrolytes can serve as stabilization of agents for the surface. Their adsorption plays a crucial role in stabilizing the particles of different concentrations of electrolyte that might otherwise be very highly abnormal[2]. The reaction is given below:

$$Fe^{2+} + 2\ Fe^{3+} + 8\ OH \rightarrow Fe_3O_4 + 4H_2O$$

3] Applications:

Imaging	Nanoparticles of iron oxide which are superparamagnetic have been used to facilitate magnetic resonance imaging (MRI). These are extremely magnetic and less dangerous. MRI utilizes nanoparticles that are smaller than 5 nm. MRI is frequently used to image inflammation, neuropathies, and cancer cells.
Targeted Drug Delivery	Researchers in modern medicine have demonstrated that iron oxide nanoparticles, which are extremely magnetic, can be employed as effective drug transporters if they are made in a way that prevents oxidation and keeps the drug molecules stable. Moreover, this stabilization will hinder the intrusion of the reticuloendothelial system (RES), thereby extending the in-vivo retention period within the circulatory system. Due to their small size, these nanoparticles have no trouble overcoming the biological barrier. Biopolymers, which are non-toxic and biodegradable, encapsulate these supermagnetic iron oxide nanoparticles to boost their bioavailability and keep them disseminated.
Tissue engineering	Super magnetic iron oxide nanoparticles with gold coating have applications in tissue regeneration and have a tendency to absorb light. Because stem cells are pluripotent, they are thought to be beneficial for tissue engineering. Repair tailored to the spot would be facilitated by coupling these with such nanoparticles. It is also possible to join other proteins to aid in the repair process.
Radiotherapy	It was discovered that the concentration-dependent enhancement of radio-sensitizing activity was possible with super magnetic iron oxide nanoparticles. Cell survival was evaluated through the clonogenic assay following radiation treatments employing brachytherapy sources and electron beams at different dosage levels.
Environmental remediation	The most prevalent heavy metal contaminants include aluminium, chromium, lead, arsenic, mercury, cadmium, and mercury. Prolonged exposure to these heavy metals can cause birth abnormalities, mental retardation, and paralysis.autism, schizophrenia, brain injury, kidney damage, weakened muscles,and might potentially result in human death. Iron oxide nanoparticles, which are extremely magnetic, were used because they provide superior molecular interaction for their tiny size.examined to see if heavy metals have been removed from water sources. It turned up that these heavy metals may be adsorbed onto the surface of these nanoparticles by electrostatic interactions, finally getting rid of the hefty elements found in the liquid phase1.

4] Size, Advantages and Disadvantages

Technique	Morphology	Advantages	Disadvantages
Lithography using e^- beam	Spherical or Rods	Precisely regulated inter-particle distance	Necessitates costly and intricately sophisticated machinery[45]
Sol-Gel method	Spheres, uneven spheres, permeable and impermeable spheres, or elongated structures	Aspect proportion, meticulously regulated in dimensions, and inner composition	Elevated permeability, frail adhesion, diminished wear resilience[46]
Hydrothermal	Extended, compact irregular spheres, and numerous shapes	The size and shape of the particle can be controlled easily	Requires high pressure and temperature[7]
Microemulsion	Spherical NPs, nanorods, hexagonal nanocrystals	Diversity of NPs	Undesirable impacts of lingering surfactants on characteristics and challenges in scaling-up processes[7]
Chemical co-precipitation	Spheres	Straightforward and efficient	Unsuitable for producing a highly pure, accurately balanced phase[8]
Biological	Tiny flakes, circular or rod-shaped orbs, asymmetrical globules	Sound replicability and scalability, substantial output, and economical expenses	Gradual and painstaking[47]

5] Conclusion: This review provides a concise discussion on Iron oxide nanoparticles exploring various synthesis methods and outlining the advantages and disadvantages. Additionally, the review covers the applications of Iron oxide nanoparticles. Among the different methods discussed, the Chemical co-precipitation method emerges to be the most efficient, cost-effective, and versatile for Iron oxide nanoparticles production, demonstrating diverse applications. However, it is noted that while co-precipitation can directly yield water-soluble Iron oxide nanoparticles, its drawbacks include sluggish crystallization and limited size control, restricting its application. Iron oxide nanoparticles are characterized by the hydrophobic nature of surface chemistry, which makes them soluble only in non-polar solvents like toluene and hexane. Despite their potential in biomedical applications,further exploration is needed to enhance their biocompatibility and reduce toxic.

References:

1: Samrot, A. V., Sahithya, C. S., Selvarani A, J., Purayil, S. K., & Ponnaiah, P. *Current Research in Green and Sustainable Chemistry*. **2020**, 4, 100042.

2: Cornell RM, Schwertmann U. *John Wiley & Sons*. **2006**, 2nd edition

3: : Srivastava, M., Chaubey, S., & Ojha, A. K. *Materials Chemistry and Physics*, **2009,** *118*(1), 174.

4: Chaturvedi, S., Dave, P. N., & Shah, N. *Journal of Saudi Chemical Society*. **2012**, *16*(3), 307.

5: De Cuyper M, Joniau M. Magnetoliposomes. *Eur Biophys J*. **1988**,15(5), 311.

6: Hasany S, Ahmed I, Rajan J, Rehman A. *Nanosci Nanotechnol.* **2012**,2(6), 148.

7: Wu W, He Q, Jiang C. *ChemInform*. **2009**;40(24):i.

8: Wu, S., Sun, A., Zhai, F., Wang, J., Xu, W., Zhang, Q., & Volinsky A. A. *Mat Lett*. **2011**,65(12),1882

9: Narayanan KB, Sakthivel N. *Adv Colloid Interface Sci.* **2010**,156(1–2):1–13.

10: Xu J, Sun J, Wang Y, Sheng J, Wang F, Sun M. *Molecules.* **2014**,19(8): 11465.

11: Maity D, Agrawal D. *J Magn Magn Mater.* **2007**,308(1), 46.

12: Sophie Laurent, Delphine Forge, Marc Port, Alain Roch, Caroline Robic, Luce Vander Elst, and Robert N. Muller. *Chem Rev*. **2008**,108(6), 2064.

13: M.K. Corbierre, J. Beerens, R.B. Lennox. *Chem. Mater.* **2005**, 17 (23), 5774.

14: A.A. Tseng, K. Chen, C.D. Chen, K.J. Ma. *IEEE Trans. Electron. Packag. Manuf.* **2003**, 26 (2), 141.

15: C.J. Jia, L.D. Sun, F. Luo, X.D. Han, L.J. Heyderman, Z.G. Yan, C.H. Yan, K. Zheng, Z. Zhang, M. Takano, N. Hayashi. *J. Am. Chem. Soc*. **2008**, 130 (50), 16968.

16: B. Lv, Z. Liu, H. Tian, Y. Xu, D. Wu, Y. Sun. *Adv. Funct. Mater*. **2010**, 20 (22), 3987.

17: V.R. Manfrinato, L. Zhang, D. Su, H. Duan, R.G. Hobbs, E.A. Stach, K.K. Berggren. *Nano Lett*. **2013**, 13 (4), pp. 1555.

18: S. Mann, N.H.C. Sparks, Richard B. Frankel, Dennis A. Bazylinski, Holger W. Jannasch. *Nature*. **1990**, 343, 258.

19: K. Revati, B.D. Pandey. *Bull. Mater. Sci.* **2011**, 34 (2), 191.

20: S. Iravani. *Green Chem.* **2011**, 13 (10), 2638.

21: N. Madubuonu, S.O. Aisida, A. Ali, I. Ahmad, T.K. Zhao, S. Botha, M. Maaza, F.I. Ezema. *J. Photochem. Photobiol. B Biol.* **2019,** 199, 111601

22: S.O. Aisida, N. Madubuonu, M.H. Alnasir, I. Ahmad, S. Botha, M. Maaza, F.I. Ezema. *Appl. Nanosci.* **2020,** 10, 305.

23: A.V. Samrot, P. Senthilkumar, S. Rashmitha, P. Veera, C.S. *J. Nanostruct. Chem.* **2018,** 8 (3), 343.

24: M. Allen, D. Willits, J. Mosolf, M. Young, T. Douglas. *Adv. Mater.* **2002,** 14 (21), 1562.

25: Lam UT, Mammucari R, Suzuki K, Foster NR. *Ind Eng Chem Res.* **2008**,47(3),599.

26: Kojima K, Miyazaki M, Mizukami F, Maeda K. *J Sol-Gel Sci Technol.* **1997**,8(1–3),77.

27: Ennas G, Musinu A, Piccaluga G, Zedda D, Gatteschi D, Sangregorio C, Stanger J.L, Concas G, Spano G. *Chem Mat.* **1998**,10(2),495.

28: Tavakoli A, Sohrabi M, Kargari A. *Chem Papers*. **2007**,61(3),151.

29: Tadić M, Marković D, Spasojević V, Kusigerski V, Remskar M, Pirnat J, Jaglicic Z. *J Alloys Comp.* **2007**,441(1),291.

30: Wang C-T, Ro S-H. *Appl Catal A Gen.* **2005**,285(1), 196.

31: Hayashi, H.; Hakuta, Y. *Materials.* **2010**, *3*, 3794-3817.

32: Hao Y, Teja AS. *J Mater Res.* **2003**,18(02),415.

33: Xu C, Lee J, Teja AS. *J Supercrit Fluids*. **2008**,44(1),92.

34: M. O'Donoghue A Guide to Man-Made Gemstones Van Nostrand Reinhold Company (1983)

35: S. Santra, R. Tapec, N. Theodoropoulou, J. Dobson, A. Hebard, W. Tan. *Langmuir*, **2001,** 17 (10), 2900. 36: J.A. Lopez Perez, M.A. Lopez Quintela, J. Mira, J. Rivas, S.W. Charles. *J. Phys. Chem. B*, **1997,** 101 (41),8045.

37: A.B. Chin, I.I. Yaacob. *J. Mater. Process. Technol.* **2007,** 191 (1–3), 235.

38: J. Vidal-Vidal, J. Rivas, M.A. López-Quintela. *Colloid. Surface. Physicochem. Eng. Aspect.* **2006,** 288 (1–3),44.

39: K. Kekalo, K. Koo, E. Zeitchick, I. Baker *MRS Online Proc. Library Archive*. **2012,** 1416

40: ElBayoumi TA, Torchilin VP, Weissig V. *Liposomes: Methods and Protocols, Volume 1: Pharmaceutical Nanocarriers.* **2010.**

41: A. Ali, H. Zafar, M. Zia, I. Ul Haq, A.R. Phull, J.S. Ali, A. Hussain. *Nanotechnol. Sci. Appl.* **2016,** 9, 49.

42. Kim D, Zhang Y, Voit W, Rao KV, Muhammed M. *J Magn Magn Mater.* **2001**,225(1), 30.

43. Kim DK, Mikhaylova M, Zhang Y, Muhammed M. *Chem Mat.* **2003**, 15(8), 1617.

44: T. Ahn, J.H. Kim, H.M. Yang, J.W. Lee, J.D. Kim. *J. Phys. Chem. C*, **2012,** 116 (10), 6069.

45: Lin X-M, Samia AC. *J Magn Magn Mater*. **2006**, 305(1), 100.

46: Laurent S, Forge D, Port M, Roch A, Robic C, Luce Vander Elst, Robert N. Muller. *Chem Rev*. **2008**;108(6), 2064.

47: Ali A, Zafar H, Zia M, ul Haq I, Phull AR, Ali JS, Hussain A. *Nanotechnol Sci Appl*. **2016**, 9, 49.