

RECENT STUDIES ON THE PROGRESS MADE IN MAGNETIC NANO PARTICLES: A REVIEW

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Abstract

Numerous uses for nanoparticles have transformed a number of societal fields. Due to its applications in specialist fields including medicine, cancer theranostics, biosensing, catalysis, agriculture, and the environment, magnetic nanoparticles in particular have attracted a lot of attention in the last ten years. The design of multi-functional Magnetic nano particles must include controlled surface engineering if the intended use is to be realized. The Magnetic nano particles have shown to be very effective as biosensors, imaging agents, drug delivery systems, and thermoelectric materials. In this review, we have first briefly covered the primary techniques of MNP synthesis before moving on to their characterisation and composition. Then, using illustrative examples, we examined the possible uses of Magnetic nano particles in various fields. We concluded by providing a summary of the present difficulties and potential futures for Magnetic nano particles. This thorough analysis not only explains the synthesis, functionalization, and use of Magnetic nano particles from a mechanistic perspective, but it also discusses their limitations and future possibilities.

Introduction

Recent developments in the area of nanotechnology have helped to progress and revolutionize a variety of industries. The number of advantages and uses for nanotechnology is expanding quickly. Nano particles (NPs) are tiny particles with typical sizes between 1 and 100 nm, which set them apart from their bulky parent materials and make them perfect for a variety of applications (Laconte et al., 2005; Cardoso et al., 2018). Magnetic nano particles (Magnetic nano particles), a nano scale substance with distinctive

magnetic characteristics, are one of them and have been extensively employed in a variety of disciplines, including biomedical, energy, engineering, and environmental applications. Due to the Magnetic nanoparticles' distinct and special features, which might be used in biomedicine, catalysis, agriculture, and the environment, they have recently attracted a lot of study attention (Hao et al., 2010; Wu et al., 2016; Thorat et al., 2017; Zhu et al., 2018; Zhang et al., 2019). Different metal elements (alone or in composites) and their oxides with magnetic properties are used to create Magnetic nanoparticles (Kefeni et al., 2017). Due to its great biocompatibility and low toxicity, super paramagnetic magnetite (Fe_3O_4) is the most widely utilized iron oxide (Assa et al., 2016; Farjadian et al., 2017). Recently, there has been a lot of focus on iron oxide Magnetic nanoparticles in order to improve and comprehend their usefulness in many fields (Bansal et al., 2017). The ideal iron oxide Magnetic nanoparticles for biological and biomedical applications are those with lower diameters (Lu et al., 2017; Mohammed et al., 2017). Superparamagnetic iron oxide Magnetic nanoparticles may be used in several applications, such as hyperthermia, magnetic resonance imaging (MRI), immunoassays, drug, and cell separation, by changing their physicochemical characteristics to change their surface chemistry (Weissleder et al., 1995; Kumar

and Mohammad, 2011). Magnetic nanoparticles have a wide range of applications in the fields of environmental, biomedical, catalysis, drug administration, and bioimaging thanks to characteristics including large surface area, metal-rich moieties, and adjustable architectures. They have been a prominent issue in recent decades due to their tunable form and size (Singamaneni et al., 2011; Purbia and Paria, 2015). Magnetic nanoparticles are now an emerging discipline of nano science and nanobiotechnology as a result of recent developments and an unprecedented volume of publications (Kudr et al., 2017; Cardoso et al., 2018; Wu et al., 2019). Magnetic nanoparticles have distinct physicochemical characteristics from their parent bulky material in terms of having a high specific surface area, which increases their superparamagnetic capabilities (Babes et al., 1999). It is essential to use nanomaterials with well defined structures to attain these features (Issa et al., 2013). Dipolar interactions, particle surface effects, size management, and other difficulties with the synthesis of monodisperse magnetic nanostructures are of major importance. However, limiting the nucleation and development of these Magnetic nanoparticles has become simpler thanks to several cutting-edge chemical synthetic techniques. As a result, the kind of surfactant and solvents utilized under various reaction circumstances greatly influence the size and structure of Magnetic nanoparticles (Xie et al., 2018). This review was created with the current interest in Magnetic nanoparticles in mind and includes a summary of recent breakthroughs in the synthesis of Magnetic nanoparticles as well as historical and contemporary investigations with their

associated benefits and drawbacks. This review's purpose is to provide information on the many classifications of Magnetic nanoparticles based on different elemental compositions and metals, as well as information on how they are used in the sectors of energy, biomedicine, biosensing, environmental protection, agriculture, and cancer catalysis. The next part also discusses the Magnetic nanoparticles' potential future difficulties.

Main Synthesis Methods of Magnetic nanoparticles

The development of various methods for the synthesis of Magnetic nanoparticles has been the subject of intense study during the last 10 years. To produce Magnetic nanoparticles with the necessary size, shape, stability, and biocompatibility, many synthetic techniques are utilized. In order to create Magnetic nanoparticles, the most popular techniques are ball milling, coprecipitation, thermal decomposition, hydrothermal, microemulsion, sol-gel, and biological approaches.

Physical Methods

The physical techniques use both top-down and bottom-up strategies. Through high intensity ball milling, the bulk materials are reduced to nanoparticle size in the top-down method. It is challenging to produce NPs by mechanical crushing that have the required form and size (Decastro and Mitchell, 2002). In contrast to the top-down strategy, the bottom-up method may produce fine, well-dispersed nanoparticles. A bottom-up strategy example is laser evaporation (Biehl et al., 2018). Magnetic nanoparticles are also created using different physical techniques such as the wire explosion method and the

inert-gas condensation method. Three physical processes ball milling, laser evaporation, and wire explosion will be covered in this study.

Ball Milling Method/Mechanical Method

A top-down method of creating Magnetic nanoparticles from bulk material is by ball milling. The mechanical grinding of particles with a coarse texture into particles with a fine texture is an easy and practical technique (Fecht et al., 1990; El-Eskandarany, 2001). This technique was first created in 1970. (Benjamin, 1970). The operation is fairly straightforward; the raw materials are contained in a little hollow cylindrical jar with plenty of steel balls acting as the grinding medium. Steel balls continuously colliding with solid materials impart kinetic energy to the solids, resulting in powder that is nano- or micron-sized. The key variables influencing the creation of nano/micro size crystals are the ball to powder ratio, ball size, vibration speed, and milling duration. The primary drawback of this procedure is the product contamination (Mohamed and Mohamed, 2019). When compared to chemically manufactured particles, the particles exhibit a broad size range.

Laser Evaporation

In a bottom-up method known as laser evaporation, nanoparticles are created by condensation from a liquid or gaseous phase (Biehl et al., 2018). The simple process of laser evaporation, also known as laser ablation, uses a high intensity laser to produce Magnetic nanoparticles. This process works well for creating iron oxide Magnetic nanoparticles (Shin et al., 2004). In this procedure, coarse-textured raw

materials (in the m or mm size ranges) are chosen and evaporated via the laser beam's focus. The material is positioned at the bottom of a cell that is filled with a liquid solution, and the laser beam is focused on it. A laser beam is used to irradiate the substance in a solution. When a substance's vapors are cooled to a gas phase, a quick condensation and nucleation occurs, which causes nanoparticles to form (Kurland et al., 2007). This process is less costly than wet chemistry procedures and does not need expensive chemicals or result in hazardous waste (Yang, 2007; Amendola and Meneghetti, 2009).

Wire Explosion Method

The wire explosion method is a brand-new physiochemical method that produces Magnetic nanoparticles in a secure and hygienic manner. This procedure is a one-step, highly productive one that doesn't call for any extra processes like NP separation from solution or byproduct re-treatment. Iron oxide Magnetic nanoparticles were previously made using this technique to remove arsenic from water (Song et al., 2013). Making less polluted nano powders using it is energy-efficient and safe for the environment (Kotov, 2003). This approach does not result in monodispersed NPs (Kawamura et al., 2015).

Chemical Methods

The many bottom-up processes used in chemical synthesis are diverse. a thorough explanation of a few popular techniques that are often used to create Magnetic nanoparticles

Comparison of Different Synthesis Methods

The synthesis of Magnetic nanoparticles has been carried out using a variety of methods. Physical, chemical, and biological procedures are the three categories into which these synthetic processes are divided. In earlier sections, we briefly examined several ways to synthesize Magnetic nanoparticles. This may assist researchers in choosing the best approach for MNP production. However, a comparison of physical and chemical approaches reveals that physical methods have difficulty producing NPs with sizes in the nanometer range (Cuenya, 2010). Through the physical method of synthesis, it is challenging to modify the particle size and form (Decastro and Mitchell, 2002). While the size and form may be altered through chemical processes by modifying certain reaction conditions (Wu et al., 2008). The hydrothermal technique is thought to be the most practical way to create Magnetic nanoparticles out of all the chemical processes. Due to its benefits in creating NPs with appropriate size, shape, high crystallinity, and uniform composition, the hydrothermal technique is flexible and outperforms alternative approaches like sol-gel and microemulsion. By reducing the likelihood of agglomeration and limiting size distribution, the hydrothermal technique enables control over the shape of produced particles (Zahid et al., 2019).

Due of its simplicity and convenience of MNP synthesis, the coprecipitation technique is used. Although the yield is great, the form control is sometimes subpar. Because the process may be finished at room temperature, the sol-gel technique offers the benefits of high purity and crystallinity, homogenous composition, and cost effectiveness.

Although it has a poor yield, the microemulsion is useful for the synthesis of monodisperse NPs with different morphologies. Compared to the coprecipitation approach, the thermal decomposition method is recommended for obtaining NPs of a smaller size. Thermal breakdown is thought to be the most effective technique so far for creating NPs with regulated size and shape (Faraji et al., 2010). When choosing a synthesis process, factors including pH, surfactant and solvent types, ionic strength, agitation, reaction duration, and stirring rate should be taken into account.

The biological technique, on the other hand, is a respectable strategy and is chosen for its high yield, cost-effectiveness, sustainability, and environmental friendliness. The development of biological synthesis in plants is still in its early stages, and the process is currently being studied (Gul et al., 2019). When compared to chemical and physical approaches, the NPs produced by microorganisms are not monodisperse, and the synthesis process is quite time-consuming (Narayanan and Sakthivel, 2010). Therefore, depending on their results and intended application, views on the technique selection may differ from researcher to researcher. For this reason, there isn't just one technique that is considered the best for creating Magnetic nanoparticles. Every approach has its limitations, and choosing one relies on a number of different things, including the yield of NPs, their morphology, size, and shape, and the cost of the experiment.

Characterization of Magnetic nanoparticles

To evaluate their physicochemical characteristics, the Magnetic nanoparticles are examined using a variety of equipment. The display of various physicochemical features of NPs depends significantly on their size. Their characteristics may be altered by even a little change in their nanoscale dimension. Atomic Force Microscopy (AFM), Energy Dispersive X-ray Diffraction (EDXD), Scanning Electron Microscopy (SEM), Fourier Transform Infrared (FT-IR) Spectroscopy, UV Spectrophotometer, Transmission Electron Microscopy (TEM), and Mossbauer Spectroscopy (MS) are a few of the tools used for their characterization (Galloway et al., 2015).

Magnetism

The creation of Magnetic nanoparticles via various synthetic techniques affects their magnetic properties. The Magnetic nanoparticles, whose sizes span from nano to micro scales, exhibit the superparamagnetic feature. These NPs exhibit magnetic sensitivity and may interact with these external magnetic fields when an external magnetic field is introduced to them (Pathak et al., 2021). However, there is no magnetism seen when there is no external magnetic field. This characteristic of Magnetic nanoparticles may enable them to be crucial components of regulated treatment and focused drug delivery. A variety of approaches with varying levels of sensitivity and information quality are used to quantify the magnetic of NPs. The net magnetization is measured using methods such as superconducting quantum interference device (SQUID) magnetometry and vibrating sample magnetometry (VSM). When examining

materials in various states, such as thin films, crystals, powders, liquids, and gases, the SQUID is helpful. Both the VSM and the SQUID are very sensitive instruments; for example, the VSM's sensitivity is 10^{-6} emu, while the SQUID's sensitivity is higher, up to 10^{-10} emu (Zahid et al., 2019). In the event that the external magnetic field is continuously applied, the SQUID and VSM may also determine the magnetic saturation and residual magnetization (Krzyminiowski et al., 2018). While the EPR (Electron Paramagnetic Resonance) method may identify the paramagnetic center and free radicals. Mossbauer spectroscopy gathers information on bonding, structural, magnetic, and oxidation state determination. When an external magnetic field is provided, the VSM can typically assess MNP magnetizations between 3 and 3 T. It is also useful in calculating the impact of the shell on the saturation of magnetism (Faraji et al., 2010). Another trustworthy method for figuring out NPs' magnetic characteristics and behavior is the Physical Property Measurement System (PPMS). This device is designed to monitor the temperature and magnetism of samples of Magnetic nanoparticles (Andersson, 2013; Singh et al., 2017).

Composition of Magnetic Nanostructures

Magnetic nanoparticles of a particular kind called iron NPs have particular magnetic characteristics. the most thoroughly investigated NPs in the realm of nanomedicine due to their magnetic properties and exceptional biocompatibility. They are reasonably priced, ecologically safe, and have high physical and chemical stability. Iron

carbonyl $[\text{Fe}(\text{CO})_5]$ previously broke down in the presence of oleic acid (OA) to create monostructure Fe NPs (Suslick et al., 1996). Because iron NPs are sensitive to oxygen, they were made using a simple aqueous phase synthesis technique that included poly (N-vinylpyrrolidone), which is helpful in preventing oxidation of the metal surface (Hou and Gao, 2004). By reducing $\text{Ni}(\text{acac})_3$ in the presence of hexadecyl amine (HDA), monodisperse nickel (Ni) NPs with an average particle size of 3.7 nm were created (Hou and Gao, 2003). Cobalt (Co) NPs with a size range of 2–6 nm were made using a bulky trialkyl phosphine reducing agent, while NPs with a size range of 7–11 nm were made with a less bulky trialkyl phosphine, demonstrating the coordination of the surfactant trialkyl phosphine with neutral metal surface sites (Sun and Murray, 1999).

Metal Alloys Magnetic Nanostructure

Metal alloy NPs with super magnetic properties are very promising. Iron-Platinum (FePt) and Iron-Palladium (FePd) are examples of nanostructured metal alloys due to their great chemical stability and magnetic crystallinity (Hou et al., 2004). FePt NPs are very valuable in biomedical applications, solution-phase synthesis, and vacuum deposition. Using adamantane carboxylic acid and tributyl phosphine as stabilizers, FePd NPs were produced at room temperature using the organic phase thermal degradation technique. The FePd NPs exhibit super magnetic characteristics with a size range between 11 and 16 nm. Previously, a wet chemical method was employed to produce monodisperse FePd NPs with a face-centered cubic (fcc) form by reducing

$\text{Pt}(\text{acac})_2$ and decomposing $\text{Fe}(\text{CO})_5$ (Sun et al., 2000). It tends to agglomerate upon conversion to fct (face-centered tetragonal). The fcc- Fe_3O_4 NPs with Mg coating were transformed to fct-FePt NPs through thermal annealing (Liu et al., 2014b). The magnesium oxide (MgO) layer prevented the NPs from aggregating. The gold-coated FePt NPs were produced by reducing $\text{Pt}(\text{acac})_2$ and decomposing $\text{Fe}(\text{CO})_5$ in octyl ether solvent. The gold coating around these NPs makes them very biocompatible (De La Presa et al., 2007). Other binary metallic alloys with strong magnetic characteristics consisting of iron and cobalt ($\text{Fe}_{12}\text{Co}_{88}$, $\text{Fe}_{40}\text{Co}_{60}$, and $\text{Fe}_{60}\text{Co}_{40}$) also exist; their oxidation is avoided by covering with gold, silver, or graphitic material (Bai and Wang, 2005; Seo et al., 2006).

Application of Magnetic nanoparticles

The Magnetic nanoparticles have attracted a lot of interest in the last 10 years due to their promising outcomes in several sectors. Magnetic nanoparticles' applicability is made more promising by their super-magnetic characteristics, distinctive size, shape, high surface area and volume ratio, and biocompatibility. These characteristics have drew many scholars from other domains to it. We have outlined the uses of Magnetic nanoparticles in this review in a number of well-known industries, including biomedicine, biosensing, environment, agriculture, and catalysis.

Biosensing

The use of Magnetic nanoparticles-based sensors has been impressive in a variety of industries, including food technology, laboratory testing, clinical diagnostics, and

environmental monitoring (Haun et al., 2010; Rocha-Santos, 2014). Particularly, the Magnetic nanoparticles-based biosensing business has attracted strong attention in the realm of nanomedicines due to biocompatibility, durability, and safety (Lin et al., 2017; Wang et al., 2017b). Magnetic nanoparticles-based biosensors have envisioned a broad applicability in the biomedical industry due to their compact size, high sensitivity, and intriguing noninvasive detection characteristic (Chen et al., 2016). Magnetic nanoparticles-based biosensors have significantly outperformed other traditional biosensors because to unique characteristics including magnetic signaling and magnetic separation. Magnetic nanoparticles may also be employed as magnetic probes to find analytes in biological samples due to the high signal-to-background ratio (Xie et al., 2011).

Due to the rising release of hazardous and deadly chemicals and compounds as a consequence of human activities, the degradation and pollution of water, soil, and atmosphere are emerging as a major environmental issue. There are several types of persistent organic pollutants in the atmosphere, such as polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), pharmaceuticals, pesticides, and industrial waste (Jones and De Voogt, 1999; Rodriguez-Narvaez et al., 2017; Richardson and Ternes, 2018). Groundwater, ocean, sewage effluents, and drinking water all include various types of organic contaminants. When these kinds of persistent organic pollutants enter the food chain, they may cause major health issues for people (Jin et al., 2014; Govan, 2020).

The development of effective technology is crucial for improving water quality.

Agriculture

Numerous studies demonstrating the effective use of metallic nanoparticles in soil quality improvement, seed germination, and plant protection (El-Temsah et al., 2016; Rui et al., 2016). For instance, iron oxide Magnetic nanoparticles may be used as soil nutrition to boost output with the least amount of drawbacks (Mishra et al., 2017). Iron is a crucial component of many physiological processes, including respiration, biosynthesis, the production of chlorophyll, and redox reactions (Rout and Sahoo, 2015). A number of crops, including peanuts, lack iron. Numerous research have been done in this area to use iron nanoparticles to treat the shortage and increase iron intake (Zuo and Zhang, 2011; Sánchez-Alcalá et al., 2014; Cheng et al., 2015; Zia-Ur-Rehman et al., 2018). Instead of being used in field circumstances, NPs are often used as nanofertilizers in hydroponic systems. The soil's most plentiful plant nutrient is thought to be iron. Its supply, nevertheless, continues to be problematic for plants.

Catalysis

Different catalytic systems and procedures have been developed up to this point for the transformation of reactants into products (Liu and Zhang, 2016). The difficulty in separating homogenous catalysts from the reactions is one of their drawbacks. Utilizing catalysts assisted by Magnetic nanoparticles, the heterogeneous catalysis constraint has recently been mitigated and eliminated. When such catalysts are separated, the Magnetic

nanoparticles combine the benefits of great dispersion and reactivity with the capacity to offer a large surface area to support active sites for reactants to be transformed into products readily (Lee et al., 2008). Magnetic materials with excellent repeatability in heterogeneous catalytic processes have been described (Martnez-Edo et al., 2018; Sudarsanam et al., 2018; Zuliani et al., 2018). The photocatalytic system has recently come into prominence as an effective and dependable technique for pollutant degradation in the presence of daylight. Sunlight acts as an external stimulation source in this system, causing it to be activated and producing free radicals that interact with contaminants to cause deterioration.

Challenges and Future Perspectives

Magnetic nanoparticles are used in a variety of industries, including biomedicine, the environment, agriculture, catalysis, and biosensing. We outlined current developments in the synthesis, characterisation, and possible uses of Magnetic nanoparticles in this study. Different MNP types with potential features are being created utilizing various synthetic techniques. These techniques include sol-gel, ball milling, thermal decomposition, hydrothermal synthesis, microemulsion synthesis, and thermal decomposition. Ball milling is a physical approach that is used to synthesize Magnetic nanoparticles in large quantities, although this process introduces contamination from the milling jars and balls. On the other hand, monodisperse Magnetic nanoparticles are made using the thermal breakdown or pyrolysis process. The pyrolysis process offers benefits since it is easy to implement and provides

excellent control over MNP size. At low processing temperatures, the sol-gel synthesis approach is employed to create Magnetic nanoparticles with uniform size distribution and enhanced stoichiometric control. The approaches listed above suggest numerous MNP types for significant biological and biomedical applications. Numerous issues, such as cancer, pollution, agricultural methods, and others, have impeded human advancement. Different types of functionalized NPs have been created throughout the years to solve these issues. By treating cancer more safely and efficiently, nanotechnology-based cancer treatment primarily rely on the effective and clever design of NPs. Due to their distinctive qualities, Magnetic nanoparticles have recently contributed more to nanomedicines. Different Magnetic nanoparticles modalities are now being studied in clinical settings for cancer cell imaging and treatments. Critical biological hurdles that Magnetic nanoparticles production and formulations must overcome include localization at the target location, efficient drug administration to the target site, cross-physiological talk, and other technical challenges unique to cancer. Clearance, endosomal escape, off-target locations, and drug efflux are some more types of obstacles. In both industrialized and developing nations, widespread bacterial resistance to antibiotics has emerged as a severe health hazard. The advent of new antibiotics and their subsequent unavailability will pose a severe concern because of numerous types of multidrug-resistant bacteria. Strategies based on Magnetic nanoparticles have been developed in the last ten years to cure infections brought on by pathogenic

bacteria and remove biofilms with the least amount of resistance. The Magnetic nanoparticles are crucial and often employed in the delivery of targeted drugs. Magnetic nanoparticles-based medication administration may lower the dosages of pharmaceuticals and thus lessen the negative effects when compared to traditional drug delivery. Additionally, since Magnetic nanoparticles naturally possess antimicrobial activity, combining them with antimicrobial compounds provides therapeutic benefits that increase the effectiveness of antimicrobial medications. Similar to this, Magnetic nanoparticles are used in wastewater treatment to remove organic and inorganic contaminants, break down colors, and kill or separate bacteria. The Magnetic nanoparticles may be used as soil fertilizers to boost yields and to control plant diseases. Research makes extensive use of the conjugation of Magnetic nanoparticles with other biomolecules, including nucleic acids, chemicals, and enzymes. In this way, a gene's transport and expression inside the host cell are effectively used. In addition to other application disciplines, heterogeneous catalysis is one area where Magnetic nanoparticles have exceptional promise. In many forms of catalysis and clean energy, magnetic NPs have been employed to coat catalysts. For the conversion of the reactants into products, the Magnetic nanoparticles may provide a large number of active sites.

Critical and helpful research is needed to develop and manufacture Magnetic nanoparticles for a variety of applications in many sectors in order to overcome obstacles. Building regulatory institutions for the secure and efficient use of

nanotechnology must be taken into consideration with advances and the development of interdisciplinary methods. To create specialized standards and platforms to advance clinical trials and pre-clinical investigations in vivo, there has to be a regular method and link between institutions and researchers. In order to effectively treat cancer and address multidrug resistance, Magnetic nanoparticles must overcome a myriad of obstacles. Discussing the ratio of magnetic NPs to catalysts is necessary. The biocompatibility and long-term toxicity of Magnetic nanoparticles are two major obstacles. The composition, morphology, size, form, structure, and side effects of Magnetic nanoparticles must all be thoroughly studied in great depth. In order to create and build Magnetic nanoparticles for a brighter future, the scientific community must overcome these kinds of massive problems and perform hassle-free clinical trials.

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