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Review Paper

Cobalt-ferrite Nanoparticles and Their Various Technological Applications: A Short Review

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Abstract— Cobalt ferrite magnetic nanoparticles have been regarded as a significant material in the field of nanotechnology for their desirable physical, chemical, magnetic, electrical and optical properties. The particles possess rich and unique magnetic properties such as high magnetocrystalline anisotropy, high coercivity, and moderate saturation magnetization etc. Easy synthesis of the particles with tunable sizes and different shapes along with chemical stability make them practically important in various technological applications. Tunable magnetic properties of the nanoparticles open up the possibility of a diverse range of useful applications such as high-density magnetic storage media, sensors, telecommunications, nano-biotechnology etc. This review article represents an overview of synthesis techniques, magnetic properties and various applications of cobalt ferrite nanoparticles including hyperthermia therapy, drug delivery, magnetic resonance imaging etc.

Keywords— Cobalt ferrite, Magnetocrystalline anisotropy, Coercivity, Superparamagnetism, Hyperthermia, Drug delivery.

1. Introduction

In recent years, magnetic nanoparticles (MNPs) have gained considerable attention among researchers due to their several useful inherent properties. Among them, spinal cobalt ferrite MNPs are of special interest. The ferrite nanoparticles (NPs) are potentially used in data storage devices [1], ferrofluids [2], magnetic resonance imaging (MRI) [3], drug delivery [4], hyperthermia therapy [5], magnetic sensors [6], permanent magnets [7] etc. Spinal ferrites have a face-centered cubic structure with a stoichiometry of MFe_2O_4 (M=metal such as Fe^{2+}, Zn^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+}, Mg^{2+}). In spinel ferrite structure the Fe^{3+} atoms occupy the sixteen octahedral positions while M^{2+} occupy eight tetrahedral positions. In the inverse spinel ferrite structure, half of the Fe^{3+} ions are located in the tetrahedral position while another half of the Fe^{3+} ions and all M^{2+} ions are located in the octahedral position [8]. Generally, cobalt ferrite ($M^{2+}=Co^{2+}$) has an inverse spinal structure however depending on the synthesis condition, the tetrahedral and octahedral positions are occupied in a different way by Fe^{3+} and Co^{2+} cations and a mixed spinal ferrite structure is formed [9, 10]. Various cation distributions lead to different oxidation states that greatly influence the magnetic, optical and electronic properties. Among the spinel ferrite nanoparticles, spinel cobalt ferrite ($CoFe_2O_4$) is most remarkable for their noble magnetic property such as high coercivity (Hc), high saturation magnetization (Ms), and large remanent magnetization (Mr). The large surface area to volume ratio of the nanostructures provides the structural degrees of freedom that induces various unique properties different from their bulk counterpart [11, 12]. Several nanostructures such as nanoparticles, nano-wires, nano-ribbons, thin films, core-shell structures, and nanocomposites of cobalt ferrite have been developed to enhance/modify the magnetic properties of the material [13-18]. The size and shape of the NPs also influence the magnetic properties drastically which can be controlled by various synthesis techniques [19, 20]. Sol-gel method [21], coprecipitation [22], hydrothermal coprecipitation [23], reversed micelles coprecipitation [24], electrochemical method etc. are most commonly used to synthesize cobalt ferrite nanoparticles (CFNPs). Several techniques are available to fabricate cobalt ferrite thin films such as sputtering deposition [25], pulsed laser deposition [26], molecular beam epitaxy [27], spray pyrolysis [28], spin coating [29], etc. Thin films of cobalt ferrite are practically important for various technological applications such as magnetic recording media, magnetic/gas sensors, microwave device applications, supercapacitors, solar absorbers, resistive switching etc [29-31]. Besides CFMNPs proved their potential in various biomedical applications. The useful applications of the nanoparticles can be found in magnetic resonance imaging, drug delivery, magnetic fluid hyperthermia therapy, bio-separation etc [32, 33].

An overview of cobalt ferrite nanoparticles (crystal structure, synthesis technique, applications) has been presented in the above section. The rest of the paper is organized as follows; Section 2 reviews recent works on cobalt ferrite nanomaterials. In section 3, comparative findings of recent work in this field have been depicted. Section 4 comprises the conclusion of this article and the future scope in this field.

2. Comparison

In thin film large perpendicular magnetic anisotropy (PMA) is required to enhance the density of magnetic recording and magnetic random access memory storage [34, 35]. The substrate-induced epitaxial strain produces a magneto-elastic effect in a uniaxial distortion that gives a large PMA in cobalt ferrite thin film. For example, cobalt-ferrite thin films grown on a MgO (001) substrate undergoing 0.5% in-plane tensile strain results in the introduction of a large PMA energy (K_u of 14.7 Merg/cm^3) [25, 36]. A similar result was also observed when thin films of cobalt ferrite were grown on a $MgAl_2O_4$ (001) substrate. A large negative K_u of 60 Merg/cm^3 was observed for 3.6% in-plane compressive strain [37]. It has been observed that the lattice strain due to the fabrication of cobalt ferrite thin film on various substrates induced a giant PMA [38]. High-coercivity cobalt ferrite nanoparticles are promising materials for their applications in magneto-optical recording media and permanent magnets. Size-dependent magnetic properties of the nanocrystalline cobalt ferrite (CF) particles make them practically important in high-density data storage devices. The coercivity (H_C) and magnetic saturation (M_S) of the magnetic nanoparticles strongly depend on domain size and shape. As the crystallite/particle size decreases the coercivity of the MNPs increases and reaches at maximum for single-domain particles at a critical diameter/size [39]. The critical single domain particle size for maximum H_C of cobalt ferrite nanoparticles is about 40 nm [24, 40, 41]. With the further decrease of particle size, the H_C decreases and becomes zero at a certain particle size. The particles show superparamagnetic behaviour. A wide range of applications can be achieved with these magnetic nanoparticles by varying H_C through tuning of crystallite size. Enhancement of H_C by various techniques such as thermal annealing [42, 43], capping [44] mechanical milling [45] etc have been reported in the literature. Small-size superparamagnetic and ferromagnetic cobalt ferrite particles have significant applications in biotechnology [46]. In hyperthermia therapy and drug delivery, ferromagnetic and/or superparamagnetic CF particles are very useful however surface modification of the particles is also necessary for those applications [47]. Recently, cobalt ferrite nanoparticles have attracted immense attention from the researcher for their latent application in water treatment. The CFMNPs are used as adsorbents and photocatalysts in wastewater treatment [48].

3. Comparative finding

3.1 Synthesis strategies of CFMNPs

Depending on technical applications various synthesis techniques have been utilized to prepare CFMNPs. Generally, for biotechnological purposes particles are prepared by hydrolytic synthesis. Under hydrolytic synthesis, there are three methods, namely coprecipitation, hydrothermal coprecipitation and reversed micelles coprecipitation. There are some advantages and disadvantages of all these synthesis methods. Spherical shape particles with sizes ranging from 10 nm to 100 nm can be prepared by the coprecipitation method. Low-cost reagents are required in this synthesis process. The surface modification of the particles prepared in this method is easy, an important criterion for biomedical use. The disadvantage of this synthesis method is broad particle size distribution [49]. Small-sized, disc and spherical shaped particles (15 nm -30 nm) with narrow size distribution can be prepared by the hydrolytic coprecipitation method [50]. To improve the size control and particle size distribution, the reversed micelles coprecipitation method is very suitable [51]. Various shapes like cubes, spheres and needles can be formed with sizes ranging from 2 nm to 80 nm in this synthesis method. However, the crystallinity of the particles is not good and the removal of surfactant used in this method is not easy. Apart from those synthesis methods, non-hydrolytic method is also significant for narrow size distribution, high size control and high crystallinity of the particles. Different shapes of particles like cubes, spheres, triangles, tetrapodes and rods can be prepared by this method. The size of the particles can also be varied in a wide range from 3 nm to 500 nm [52]. Mechanical milling is a process to enhance magnetic properties in the CFMNPs. The high density of defects and high level of strain produced by milling in the CFMNPs induce large coercivity [53]. To induce high coercivity in the CFMNPs, capping with suitable material also plays an important role [24]. A high coercivity of 9.47 kOe was observed by Limaye et al. in oleic acid-capped chemically synthesized CFMNPs of crystallite size ∼20 nm [54]. The core-shell structures of cobalt ferrite nanoparticles have been studied widely for hyperthermia therapy [55, 56]. Mesoporous cobalt ferrite/hydroxyapatite core-shell nanocomposites have been prepared by Hassanzadeh-Tabrizi et al. and they investigated the compatibility of the nanocomposites for hyperthermia and drug release applications [57].

3.2 Various applications of CFMNPs

Cobalt ferrite ($CoFe_2O_4$) is a significant hard magnetic oxide owing to its several potential applications such as in high-density magnetic recording, magnetic random access memory storage, magneto-optical and magneto-electric devices as well as in the biotechnological field [58-61]. The nanosized magnetic materials have unique magnetic properties which have a striking dependence on their size. Besides, the interaction among the particles strongly influences the magnetic properties of the MNPs. In recent years great attention to MNPs has been focused because of the opportunity to modify the magnetic properties of the particles by controlling the size, shape and cation distribution [62]. The large coercivity and magnetic remanence of cobalt ferrite MNPs have opened a new opportunity to be utilized as permanent magnets as they duplicate the properties of Alnico permanent magnet alloys [63]. Recently cobalt ferrite nanomaterials have been considered as a promising gas-sensing element for their temperature-dependent surface morphology and electronic structure [64]. Recently, Xiangfeng et al. [65] investigated the gas-sensing properties of cobalt ferrite nano-crystallites synthesized via hydrothermal route for the sensing of ethanol. The biocompatibility and antibacterial property of the cobalt ferrite NPs makes them a suitable option for antibacterial uses in the industrial, food, and medical fields [66-68]. Doping with rare earth elements (La, Ce, Sm, Gd, Dy and Er) in CFMNPs has opened a new area of research as it modifies the structural, magnetic and dielectric properties of the material significantly. A suitable amount of trivalent Gadolinium substitution in cobalt ferrite nanomaterials enhances its magnetic and electrical properties which makes it a promising material to be used in high-density storage devices [69-71]. The rare earth ions have a higher tendency to occupy the octahedral position (B-site) in the spinel structure owing to their large size. However, there are some reports in the literature where a decrease of H_C and M_S was observed while doping with rare earth elements perhaps due to dilution of magnetic moments [72]. Besides, Ni, Mn, Al, In, etc. other elements were substituted in cobalt ferrite to explore the magnetic, optical and electric properties [73-75]. Nowadays, there is an increasing interest in the application of CFMNPs in biomedicine. The rapid development of nanotechnology has made a huge impact in the field of nanoparticle-based biomedical applications. Utilizing the properties of the MNPs, various technological applications have been developed such as magnetic resonance imaging (MRI), bio-separation, biosensing, bacteria detection and sequestration by magnetic capture, monitoring stem cell migration, hyperthermia, drug delivery etc [76, 77]. CFMNPs are effective in diagnostic and therapeutic applications in the field of biology as they are biocompatible. In hyperthermia therapy and drug delivery, the CFMNPs are also promising material. However, this kind of application requires surface coating/ functionalization of the particles [78-80].

4. Conclusion and future scope

With the advancement of nanoscience and nanotechnology, cobalt ferrite MNPs have explored its many facets. Several new synthesis methods have been developed based on their applications, which led to the development of cobalt ferrite with graceful properties. In addition, the application of cobalt ferrite MNPs have been explored in various growing fields such as biomedicine, catalysis, permanent magnets, sensors etc. Recently the implementation of CFMNPs in water purification utilizing the property of adsorption and photocatalysis has become a growing field of interest. The application of cobalt ferrite nanomaterials in the biomedical field is a growing field of interest. However, for clinical application of the CFMNPs the properties like cytotoxicity, biodegradability, adsorption, distribution, metabolism and elimination are of great concern. A lot of basic and clinical research needs to be done to make these applications/technologies a useful tool in the near future.

Conflict of Interest

The author declares no conflict of interest.

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