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Progress, Challenges and Opportunities in Divalent Transition Metal-Doped Cobalt Ferrites Nanoparticles Applications

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Abstract

Engineered nanomaterials with tailored properties are highly required in a wide range of industrial fields. Consequently, the researches dedicated to the identification of new applications for existing materials and to the development of novel promising materials and cost effective, eco-friendly synthesis methods gained considerable attention in the last years. Cobalt ferrite is one of the nanomaterials with a wide application range due to its unique properties such as high electrical resistivity, negligible eddy current loss, moderate saturation magnetization, chemical and thermal stability, high Curie temperature and high mechanical hardness. Moreover, its structural, magnetic and electrical properties can be tailored by the selection of preparation route, chemical composition, dopant ions and thermal treatment. This chapter presents the recent applications of nanosized cobalt ferrites doped or co-doped with divalent transition ions such as Zn^{2+} , Cu^{2+} , Mn^{2+} , Ni^{2+} , Cd^{2+} obtained by various synthesis methods in ceramics, medicine, catalysis, electronics and communications.

Keywords: cobalt ferrite, doping, transition metal, nanoparticles, applications

1. Introduction

In the last decades, a wide range of nanomaterials were developed for applications in the field of magnetic recording and imaging, data and energy storage, refrigeration, electrical and communication devices, environmental depollution, catalysis, ceramics and pigments, sensors, medicine, etc. [1–8].

Spinel ferrite nanoparticles (NPs) with a general formula of MFe_2O_4 (M = divalent metal ion such as Mn, Cu, Co, Ni and Zn) have opened a new and exciting research field because of their unique structural, magnetic, optical and electric properties. Among them, nanosized Co ferrite received a lot of attention due to its remarkable mechanical and chemical stability, wear resistance, dielectric character, electrical conductivity and excellent magnetic properties

such as high coercivity (H_C) and moderate saturation magnetization (M_S), high Curie temperature (T_C) and large magnetocrystalline anisotropy [8, 9]. It also possesses some other unique characteristics such as good catalytic performance, small particle size, large surface area, narrow optical bandgap, non-toxicity and low production costs [10]. Depending on the composition, synthesis method and thermal treatment, Co ferrites have different structural, optical, electric, magnetic and biomedical properties [4, 11].

The doping with different elements adjusts the properties of ferrites by changing the structure, crystallinity and elements distribution among tetrahedral (A) and octahedral (B) sites [10]. The dopant amount, valency, size and site preferences define the structural, electrical and magnetic properties of doped Co ferrites [12]. The Co ferrite has an inverse spinel structure, but the doping with divalent metal ions could change its structure into normal spinel [13]. The change from normal to inverse spinel depends also on the ratio between Co and the dopant ion. Co ferrite is a hard-magnetic material, but it may be softened by doping with non-magnetic ions [14].

The NPs embedding into or coating with insulating matrix such as silica could also considerably change the properties of the obtained nanocomposites (NCs), as the silica network can limit the particles growth, act as a buffer to protect the nanoparticles from mechanical stress and minimize the surface roughness and spin disorder [1]. Thus, by selecting the dopant, synthesis route and parameters, nano-sized doped Co ferrites with tailored properties were produced for a broad range of applications [9, 12].

Various methods for the preparation of undoped and doped Co ferrite NPs have been reported such as: sol-gel, co-precipitation, polymerized complex, hydro-thermal, thermal plasma methods, sol-gel, solvothermal, thermal decomposition, ultrasonic cavitation, mechanical alloying, ball milling, pulsed laser deposition, reverse micelle, micro-emulsion, microwave assisted synthesis, thermal decomposition, electrochemical and auto-combustion [6–8, 15, 16]. Although by using these methods, the required sizes and microstructures can be achieved, they are difficult to apply on large scale due to their complex and expensive procedures, long reaction times, high reaction temperatures, hazardous reagents and by-products and potential harm to the environment [16]. Among different synthesis procedures, the sol-gel method and post-annealing treatment is one of the simplest, feasible and most effective routes that produces high purity NCs at low temperatures and permits a good control over the particle size, morphology and chemical composition [1].

In this review, we summarize the recent, significant developments related to applications of Co ferrite NPs doped with divalent transitional metals in different fields based on their coloristic, magnetic, antimicrobial, biological, catalytic and dielectric properties.

2. Applications of coloristic properties

The conventional coloring method of ceramics is based on the addition of pigments or dyes. Generally, the ceramic pigments are crystalline inorganic transition metal oxides powders with high chemical and thermal stability. They are soluble in glasses and glazes at high temperatures, have high tinting strength, high refractive index, low abrasive strength, and acid and alkali resistance. The color of pigments is determined by the presence of chromophore ions (usually transition metals) in an inert matrix (oxidic systems) or these ions may be part of their own matrix, as in the case of ferrites. The nano-pigments (nanoparticles dispersed in an organic vehicle) have a wide range of applications due to their high

surface coverage, sharp spectral features, high scattering and uniform dispersion [17, 18]. The color performance of conventional ceramic pigments depends on the coloring efficiency and dissolution kinetics in the ceramic matrix, that are expected to be improved by small particle sizes. Magnetic inorganic pigments are also used in high-tech applications such as radar absorbing materials in military applications [2, 3].

Co ferrite is a black pigment widely used in the ceramic industry due to its excellent properties such as chemical and thermal stability [17]. There are only few studies reporting the use of divalent transition metal doped Co ferrites NPs as pigments. Sol-gel synthesis followed by post annealing pathway was used to obtain Zn doped Co ferrites ($\text{Co}_{0.3}\text{Zn}_{0.7}\text{Fe}_2\text{O}_4$ and $\text{Co}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4$) embedded in SiO_2 matrix in order to be used as dark gray to black color ceramic pigments [19]. The coloring properties of the $\text{Zn}_{0.6}\text{Co}_{0.4}\text{Fe}_2\text{O}_4$ NPs were tested by embedding in opaque and transparent tile glazes, and their application on ceramic tile. For pigments, the cartesian coordinates confirmed the dark gray color, that becomes almost black in bulk, while by dispersion in glazes the dark pigment present a bright gray color [20].

3. Applications of magnetic properties

The magnetic properties of nanomaterials, associated with the spin of electrons, make them suitable for various applications in biotechnology, telecommunications and electronic industries. The magnetic properties of cubic spinel ferrites depend upon their metallic composition, particle size and cationic distribution between tetrahedral (A) and octahedral (B) sites [7, 21]. In case of magnetic NPs, the presence of large number of atoms at the surface due to high-surface-to-volume ratio and finite size effects result in several interesting and superior properties compared to bulk materials [22].

Co ferrite is well-known magnetic nanomaterial with high H_C and M_S . The M_S , H_C , T_C and anisotropy constant (K) of Co ferrite decrease by doping with non-magnetic ions decrease the hard-magnetic behavior and change the ferromagnetic to superparamagnetic behavior, leading to various applications [14, 23, 24].

Zn doped Co ferrites are soft magnetic materials with good chemical stability and high H_C [25]. The H_C , remanence magnetization (M_R) and squareness ratio (M_R/M_S) decrease by doping, as a result of the anisotropic nature of spinel Co-Zn ferrites and the non-magnetic moment of Zn^{2+} ions. The M_S values increase with the increasing content of dopant ions and their preference for tetrahedral (A) site. The dopant ions displace Fe^{3+} from tetrahedral (A) to octahedral (B) sites, resulting in weak magnetic interactions and low Neel temperature. High content of Fe^{3+} and Co^{2+} magnetic ions at the octahedral (B) sites leads to enhancement of B-B exchange interaction and weakening of A-B interaction. Nanosized magnetic zinc-cobalt ferrites with different Co to Zn ratio were obtained by co-precipitation [24], auto-combustion [13] and sol-gel [14] methods. The high M_S values make Zn-Co ferrites potential candidate for high-frequency inductors, information technology and communication [25].

In case of $\text{Co}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ ($x = 0, 0.1$) obtained by auto-combustion, the co-doping with diamagnetic (Zn^{2+} and Cd^{2+}) ions brings interesting change in the magnetic properties of Co ferrite. The Zn-Cd co-doped Co ferrites ($\text{Zn}_x\text{Cd}_{0.375-x}\text{Co}_{0.625}\text{Fe}_2\text{O}_4$, $x = 0.0, 0.075, 0.125, 0.25$) synthesized via chemical co-precipitation route are recommended as soft magnets. The variation of M_R , M_S and H_C is due to the different chemical composition, crystal structure, particles size and arrangements at the lattice sites. The H_C also decreases by increasing Zn content, due to the lower magneto-crystalline anisotropy of Zn compared to Co and Cd [21].

The magnetic properties of $\text{Co}_{1-x-y}\text{Sr}_x\text{Zn}_y\text{Fe}_2\text{O}_4$ ($x = 0.0, 0.01, 0.05, 0.3$ and $y = 0.0, 0.05, 0.1, 0.4, 0.5, 0.7$) NPs synthesized by spontaneous gel auto-combustion (Pechini) technique were strongly influenced by the presence of both dopant ions, resulting in a superparamagnetic behavior [23]. The decrease of M_S values with increasing dopant ions content and decreasing particle size is due to the surface anisotropy of nanoferrites, while the decrease of H_C values is the result of some structural defects, such as dislocations, grain boundaries and anisotropy. The obtained results recommended the Zn-Sr co-doped Co ferrite as excellent candidate for various applications such as information storage devices, contrast agents in magnetic resonance imaging and gas sensors [23].

The addition of surfactants assures the control of the crystal nucleation and growth, due to their capability to act as a protective coating for NPs, reduces coalescence and enhances the crystallite size, porosity and specific surface. All these parameters further allow the control of the magnetic properties. In this regard, $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ NPs prepared by co-precipitation method with ethanol as a surfactant show good M_S and large H_C [13]. When Co^{2+} ion with higher magnetic moment replaced Ni^{2+} ion with lower magnetic moment at B-sites, the H_C and M_R of $\text{Co}_x\text{Ni}_{1-x}\text{Fe}_2\text{O}_4$, ($x = 0.0-0.4$) [26] and $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0, 0.25, 0.5, 0.75, 1.0$) [27] increased, while M_S changed randomly. This increase is the result of cations distribution at the octahedral (B) and tetrahedral (A) sites in lattice structure, in spin canting and spin disorder [26, 27]. The $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ ($x = 0.0, 0.15, 0.3, 0.45, 0.6, 0.75, 0.9, 1.0$) synthesized by Pechini's sol-gel method showed an increase of M_S , H_C and T_C by Co^{2+} doping. Also, the number of magnetic domains increases and domain wall movement is facilitated by increasing particle size [28].

The magnetic properties of Co ferrite are also modified by incorporating Mn^{2+} ions. In case of $\text{Mn}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.2, 0.4, 0.6, 0.8$) synthesized by sol-gel precipitation method, the M_S increases (up to $x = 0.4$) and then decreases (up to $x = 0.8$) with increasing Mn^{2+} content, due to the surface disorders resulted from the distortion of the magnetic moments at the surface and to the antiferromagnetic nature of the Mn^{2+} ions. The K decreased with increasing Mn^{2+} content, indicating the interaction between grains [29]. The M_S and magnetic moment increase with increasing Co^{2+} content in $\text{Mn}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ ($x = 0.2, 0.4, 0.6, 0.8$) obtained by auto-combustion the ferrite structure [7].

4. Applications of antimicrobial activity

Nowadays, the alternative antimicrobials are highly considered due to the intense growing bacterial resistance towards conventional drugs [30]. In this regard, the development of novel multifunctional materials with antimicrobial properties that meet the requirements of a drug delivery system allowing the minimization of antibiotic concentration is of great interest. The essential characteristics of ferrite nanoparticles such as the high surface-to-volume ratio and nanoscale particle size, improve their reaction with pathogenic microbes. Also, the high surface area, low crystallite size and porosity have a significant role in improving the efficiency of NPs even at low (20 ppm) concentrations [31]. The main drawbacks in the use of these materials are that their antimicrobial properties easily change by varying their size, shape and crystallinity [32].

There are only few studies that investigate the antimicrobial effect of transition metal substituted Co ferrite nanopowders. Zhang et al. reported that the bactericidal effectiveness against gram-negative *E. coli* bacteria of $\text{Cu}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0, 0.3, 0.5, 0.7, 1.0$) NPs prepared by wet chemical co-precipitation method was enhanced by increasing Cu content [33]. The mechanisms involved in the

antibacterial activity of NPs are: (i) decomposition of ferrite and formation of reactive oxygen species, (ii) electrostatic interaction of nanomaterials with cell membrane and (iii) photocatalytic light activation of nanoparticles [34–37]. The particle size, morphology, surface area, increase in oxygen vacancies, chemical molecule diffusion ability and discharge of metal ions also play important roles in the bactericidal activity [38]. Good antibacterial activity against *E. coli* and gram-positive *S. aureus* of $\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_{1.9}\text{Bi}_{0.1}\text{O}_4$ NPs synthesized by combustion technique was obtained, due to the co-doping of Cu and Bi in Co ferrite [39].

The bacterial growth rate inhibition of Zn-substituted Co ferrite ($\text{Zn}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$, $x = 0.0, 0.5, 1.0$) nanoparticles (NPs) obtained via sol-gel route was found to be higher for the methicillin-resistant *S. aureus* (MRSA) than for *E. coli* strains [40]. Oppositely, the antibacterial activity of the $\text{Zn}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0, 0.3, 0.5, 0.7, 1.0$) NPs obtained by sol-gel process using citric acid as chelating agent was higher against gram negative bacteria (*E. coli*) than against gram-positive bacteria (*S. aureus*). Generally, the antibacterial capacities increased with increasing Zn content [41]. The *in vitro* antimicrobial activity of $\text{Co}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ prepared by citrate-gel method tested against a wide range of gram-positive (*B. subtilis*, *S. aureus*, *M. luteus*) and gram-negative (*E. coli*, *P. aeruginosa*, *K. planticola*) bacteria revealed its efficiency in treatment of plants and trees affected by large microbial cells [42]. Good antibacterial effects of Zn-doped Co ferrite NPs prepared using curd as fuel via combustion method against gram-negative *S. typhi* and gram-positive *S. aureus* was also reported [43]. The obtained result indicated that Zn doped Co ferrite may be used as component in cosmetics, emulsions, creams, powders and lotions for dermatological and biomedical treatments (drug carriers, magnetically directed drug delivery, imaging factors and cancer therapy) [35].

The bactericidal activity of $\text{Co}_{0.5}\text{Fe}_{0.5}\text{Fe}_2\text{O}_4$ and $\text{Co}_{0.2}\text{Fe}_{0.8}\text{Fe}_2\text{O}_4$ NPs with average particle size of 5.0–6.4 nm, has been studied against gram-negative (*E. coli*), gram-positive (*S. aureus*), bacteria and fungi (*C. parapsilosis* and *C. albicans*), pathogens known to increasing mortality associated with multidrug resistance [5, 44]. $\text{Co}_{0.2}\text{Fe}_{0.8}\text{Fe}_2\text{O}_4$ NPs exhibited good antibacterial efficiency (21–70%) against all tested microorganisms. The number of colonies decreased considerable with increasing Co content in the investigated NPs [5].

$\text{Mn}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ ($x = 0.2, 0.4, 0.6, 0.8$) prepared using open-air auto combustion was found to have excellent antifungal activity against *Rhizopus fungi* and its efficiency increase with increasing Co content [7]. Ashour et al. demonstrated the antimicrobial activity of metal (Zn, Mn, Cu) doped Co ferrite nanoparticles against *B. subtilis*, *S. aureus*, *E. coli*, *P. aeruginosa* and *C. albicans*. The Zn-substituted Co ferrite NPs, were more active against gram-positive than gram-negative bacteria and had strong antifungal activity against *C. albicans*. Gamma-irradiated Zn-substituted Co ferrite (150 kGy) was more active against *S. aureus* and *P. aeruginosa*, as a result of the decreasing crystallite size [35].

The $\text{M}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($\text{M} = \text{Zn, Cu, Mn}$; $x = 0.00, 0.25, 0.50, 0.75$) NPs synthesized via sol-gel method were investigated as antibacterial agents towards bacteria that commonly diffused on the surfaces of the medical operating room walls (*S. lentus*, *S. sciuri*, *S. vitulinus*, *S. aureus*, *A. viridians* and *E. columbae*). The antibacterial activity is enhanced in the following order: $\text{Mn}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4 > \text{Cu}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4 > \text{Zn}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$. The most effective ferrite was $\text{Zn}_{0.75}\text{Co}_{0.25}\text{Fe}_2\text{O}_4$ NPs which exhibited the highest activity towards all investigated pathogenic bacteria. The highest activity of $\text{Mn}_{0.75}\text{Co}_{0.25}\text{Fe}_2\text{O}_4$ was against *S. vitulinus*, while $\text{Cu}_{0.75}\text{Co}_{0.25}\text{Fe}_2\text{O}_4$ NPs were effective against *S. aureus* [31].

The antimicrobial performance of $\text{M}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$; ($\text{M} = \text{Zn, Cu, Mn}$; $x = 0, 0.5$) NPs prepared using a sol-gel method in the presence of citric acid and ethylene glycol upon pathogenic microorganisms infected urinary tract and blood samples was

investigated by Maksoud et al. The tested pathogens were gram-positive bacteria (*S. epidermidis*, *S. aureus*, MRSA and *E. faecalis*, *B. subtilis*), gram-negative bacteria (*A. baumannii*, *E. cloacae*, *E. coli*, *K. pneumoniae*, *P. aeruginosa*) and uni-cellular fungi (*C. albicans*). Zn-Co ferrite NPs displayed a maximum growth inhibition against *K. pneumoniae*, *P. aeruginosa* and *C. albicans* [30].

The antimicrobial activity of co-doped $\text{Co}_{0.5}\text{M}_{0.5}\text{Fe}_2\text{O}_4$ NPs ($\text{M} = \text{Cu, Zn, Mn, Ni}$) obtained by the sol-gel process using citric acid as the chelating agent tested against *E. coli* and *S. aureus* revealed that substituted Co ferrite NPs exhibited the most effective biocidal property, while the substitution of Zn and Cu in Co ferrite NPs considerably enhanced the antibacterial activity [45].

5. Applications of biological properties

The applications of nanotechnology in various medical areas, especially in drug delivery have been extensively explored lately. Considering the ultra-small (1–100 nm) and controllable size, high surface-to-mass ratio and high reactivity of NPs, they easily interact with biological systems [46].

The nanosized spinel ferrites and transition metal-substituted ferrites could successfully substitute some antibiotics that are currently used to combat pathogenic bacteria in the gastrointestinal tract of animals, as well as other biomedical applications. Many studies reported the synthesis and characterization of transition metal substituted Co ferrite NPs, but the attention dedicated to their biocompatibility in view of *in vivo* biomedical applications to assure their safe clinical use is still limited. The key criteria for their clinical applications are good biocompatibility and safety [47].

The use of magnetic nanoparticles in biomedical applications demands appropriate shape and size, high magnetization, good ability to deliver the pharmacologically active compounds, non-toxicity and biodegradability. The overall biocompatibility of $\text{Co}_{0.5}\text{M}_{0.5}\text{Fe}_2\text{O}_4$ ($\text{M} = \text{Cu, Zn, Mn, Ni}$) NPs synthesized by the sol-gel process using citric acid as chelating agent decreased in the following order: $\text{Co}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4 < \text{Co}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4 < \text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4 < \text{Co}_{0.5}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4$. The biocompatibility of NPs depended on the toxicity of transition metal and the releasing rate of transition metal ions into the cell culture medium [48]. Some possible mechanisms of magnetic NP-based antimicrobial drug delivery to microorganisms could be: (i) the NPs fuse with microbial cell wall or membrane and release the carried drugs into the bacteria cell; (ii) the NPs bind to cell wall and continuously release the drug, which diffuses into the interior of the microorganisms [49]. Iqbal et al. reported the development of $\text{Zn}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ NPs, with the required shape and size, as anti-cancer drug with passive targeting NPs delivering system into cancerous cells by applying photodynamic therapy through controlling the particle size according to the human body (HepG2) cells [40].

The applications of ferrites in tissue engineering are limited due to their inertness towards bioactivity and release of some toxic elements into the human body fluid. However, the migration can be controlled by encapsulation of ferrite NPs by glass matrix. The addition of bioglass in the ferrite displays some biodegradability and supports better osteoblasts growth *in vitro*. In this regard, the bioactive glass containing $\text{Co}_{0.2}\text{Cu}_{0.8}\text{Fe}_2\text{O}_4$ prepared using self-propagating high-temperature synthesis, showed good potential in bone hyperthermia application [50]. In magnetic hyperthermia, the ferrite NPs are used as local heat dissolving agents in external magnetic field. After their introduction into the body through blood, the body's immune system identifies them as foreign substances and the body rejects the material. To overcome this problem, the

biocompatible surface-coating (i.e. chitosan) helps to stabilize the ferrite NPs and provides an available surface area for the biomolecular conjugation for biomedical applications [51]. In this regard, the study of the effect of chitosan-coated $\text{Co}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$) NPs obtained via wet chemical co-precipitation on the hyperthermia temperature (directly related to specific loss power for cancer treatment) revealed that $\text{Co}_{0.2}\text{Mn}_{0.8}\text{Fe}_2\text{O}_4$ exhibited hyperthermia range [52].

6. Applications of catalytic activity

The catalysts are important players in numerous chemical processes, especially in organic synthesis or decomposition of persistent pollutants. In the last decade, the use of magnetic NPs as catalysts attracted considerable interest due to the enhancement of the reaction speed, possibility of catalyst separation from the reaction medium by using an external magnet, without any filtration or centrifugation, and its reuse or recycling [53, 54]. In this regard, several conventional synthesis methods were replaced with more eco-friendly options that use magnetic nano-sized catalysts. The catalytic processes that use magnetic NPs as catalysts include decomposition of recalcitrant organics, dehydrogenation, oxidation, alkylation and coupling reactions [9, 54].

The catalytic activity is influenced by the particle size, surface area, morphology, nature and concentration of the catalyst [10, 53]. In spinel ferrites, the presence of cations with different charges determines its catalytic properties as it allows internal redox reactions [55]. The distribution of metal ions between tetrahedral (A) and octahedral (B) sites also influences the catalytic activity. Thus, by doping transition metal ions in the ferrite structure, the cationic distribution is changed resulting in modified catalytic activity [10].

One of the main applications of magnetic NPs as catalysts is in the photocatalytic degradation of organics in the presence of visible or UV light. The photocatalytic activity of NPs is based on their capacity to efficiently absorb photons, that excite electrons from the valence band into the conduction band, leaving positively charged vacancy to react with the water molecules and to generate active radicals such as hydroxyl ($\cdot\text{OH}$) or superoxide ($\cdot\text{O}_2$) that further react with the pollutants [56]. Beside the ability to absorb photons, the reusability, recyclability, low cost, chemical stability and high corrosion resistance are important factors in the selection of photocatalysts [57]. The crystallite size, surface area, band gap, cations distribution among tetrahedral (A) and octahedral (B) sites and magnetic properties are influenced by the dopant type and amount [10, 43].

In the last decades, a wide range of non-biodegradable organic dyes, inks and pigments were identified in wastewaters from the leather, textile, printing, paper, food and cosmetics industries. These dyes may pose carcinogenic and mutagenic risks and are difficult to treat using conventional water treatment methods. Nanosized Co ferrite is a magnetic material with high H_C and moderate M_S , narrow band gap, low toxicity, low price and good catalytic activity [10, 58]. By doping, its structural and catalytic properties may be further enhanced. The doped and co-doped Co ferrites are promising catalysts that may decompose recalcitrant organic chemicals from wastewaters or enhance the synthesis of organics [9, 52, 56, 59–61]. The doping of transition metal ions (Cr, Mn, Co, Zn) into the spinel lattice of Co ferrite influences the physicochemical properties and improves their stability [11]. Moreover, the doping favors the formation of mixed or inverse spinel structures and introduces new donor or acceptor levels, which boosts the visible light activated photocatalyst activity [62].

The photocatalytic activity of a wide range of doped Co ferrites were tested on rhodamine B (RhB), methyl orange (MO), methylene blue (MB) and congo red (CR), synthetic dyes known to be highly toxic and carcinogenic. Nanocrystalline magnetic $\text{Zn}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$) with good photocatalytic activity was obtained by reverse micelle technique [63]. The doping with Zn increased the RhB degradation rate and reduced the degradation time, while, the band gap increased with increasing Zn content [63]. The photocatalytic degradation of CR and Evans blue by $\text{Zn}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0, 0.2, 0.4, 0.6$) prepared using curd as a fuel through the combustion method was found also to increase with the increase of Zn doping up to $x = 0.4$, suggesting that Zn doped Co ferrite are better photocatalysts than Co ferrite [43]. The photocatalytic activity of $\text{M}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($\text{M} = \text{Zn, Cu, Mn}$; $x = 0.0, 0.25, 0.50, 0.75$) NPs synthesized by citrate sol-gel method enhanced with increasing M content, but were lower than that of undoped Co ferrite in case of $\text{M} = \text{Cu}$ and Zn and higher in case of $\text{M} = \text{Mn}$ used for MB degradation [31].

The photocatalytic performance of $\text{Co}_{0.6}\text{Zn}_{0.4}\text{Cu}_x\text{Fe}_{2-x}\text{O}_4$ ($x = 0.2, 0.4, 0.6, 0.8$ and 1.0) obtained by sol-gel auto combustion method was evaluated by MO dye degradation under visible light and presence of hydrogen peroxide. The results showed that the degradation of MO enhances as the content of Cu in Co-Zn ferrites increases, due to the strong preference of Cu^{2+} ions for the octahedral (B) sites [61]. The photocatalytic degradation of CR by $\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_{1.9}\text{Bi}_{0.1}\text{O}_4$ NPs obtained by solution combustion technique was found to have around 90% efficiency, the photocatalyst being stable and reusable [39]. High removal percentage of CR and bisphenol A was reported for $\text{Co}_{0.5}\text{Cu}_{0.5}\text{Fe}_{1.95}\text{Ce}_{0.05}\text{O}_4$ after exposure to both visible and UV-light [64].

The $\text{Zn}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ ($x = 0.03, 0.1, 0.2$) and $\text{Cu}_x\text{Co}_{0.5-x}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4$ ($x = 0.1, 0.2, 0.3, 0.4$) NPs obtained by facile reduction-oxidation route and respectively precipitation method in the presence of oleic acid as a surfactant, were found to be able to photodegrade MB, the degradation efficiency decreasing with the increase of Zn and Cu content, respectively [57, 65].

Despite the high number of applications of transitional metal doped Co ferrites in the photocatalytic decomposition of various organic pollutants, there are only few studies on their use in organic synthesis. The Ni-substituted Co ferrite NPs supported on arginine-modified graphene oxide nanosheets ($\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4@\text{Arg-GO}$) were proven to be effective for the one-pot tandem oxidative synthesis of 2-phenylbenzimidazole derivatives [66]. $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$) ferrite NPs obtained by microemulsion method were found to effectively reduce 4-nitrophenol to 4-aminophenol in the presence of NaBH_4 as reducing agent [67].

Another important application of magnetic spinel NPs is in the field of renewable energy production and storage as catalysts for driving the water electrolysis by enhancing the hydrogen and oxygen evolution reactions (HER, OER). Ni-Co ferrite ($\text{Co}_{0.5}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4$) anchored on ultrathin conductive graphene oxide nanosheets acts as a highly active, stable and low-cost electrocatalyst in the water splitting processes, being a low-cost alternative to noble metal-oxides catalyst [68]. The OER and HER catalytic activity of $\text{Co}_x\text{Ni}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0, 0.25, 0.5, 0.75, 1.0$) NPs prepared by citric acid assisted sol-gel combustion method was found to be lower than bulk Ni ferrite, the Ni content increase improving the catalytic activity and the electron transfer rate [69].

7. Applications of dielectric properties

The significant progress in information technology, electronics and wireless communication devices together with a new trend of miniaturization and

multifunctionality led to the necessity of new materials with special characteristics. Considering the structural, electric and magnetic properties, the nanosized ferrites may become important candidates for applications in microwave communication systems, electromagnetic devices, resonators and filters for satellites, broadcasting equipment, batteries, supercapacitors and many other microwave devices [70].

The dielectric structure of ferrites consists in well conducting grains separated by highly resistive grain boundaries. The resistive grain boundaries are more effective at low frequencies, while the highly conducting grains act at high frequencies [29]. The dielectric constant at low applied frequencies is determined by the space charge polarization favored by the electrons grouped along the resistive grain boundary [6, 29]. In case of doped Co ferrites, the dielectric constant depends on the content of Fe^{3+} , Co^{2+} and other divalent transition ions present in the spinel structure [6]. Generally, the dielectric properties are strongly influenced by the grain size, porosity, synthesis method and annealing temperature [6, 29].

Considering its good chemical and thermal stability, high electrical resistivity, magnetic anisotropy, high H_C , moderate M_S , superparamagnetism, ferrimagnetism and dielectric structure, the Ni doped Co ferrite is a good candidate for microwave devices and data storage [71]. The $\text{Co}_{1-x}\text{Ni}_x\text{Fe}_2\text{O}_4$ ($0.0 \leq x \leq 1.0$) synthesized using simple, low temperature auto-combustion method showed high resistance. As the Ni content increases, the dielectric constant and loss tangent decrease and remain constant at higher frequencies, while conductivity increases with increasing frequency [71]. The use as supercapacitors of mixed ternary Cu-Co-Ni ferrites obtained by sol-gel synthesis and citric acid as chelating agent was investigated by Bhujun et al. [72]. The cyclic voltammogram profiles showed that the capacitive behavior is close to ideal rectangular shape, confirming the reversibility of the system and the decrease of specific capacitance value with the increase of the cycle numbers. The specific capacitance of $\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ (221 Fg^{-1}) was higher than of $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ (60 Fg^{-1}) and showed excellent cycling stability [72].

$\text{Mn}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.2, 0.4, 0.6, 0.8$) NPs synthesized by sol-gel precipitation method have dielectric properties that decrease with the increase of the doping ratio for $x = 0.2-0.6$ [29]. However, the $\text{Mn}_{0.8}\text{Co}_{0.2}\text{Fe}_2\text{O}_4$ was found to have the highest dielectric constant (8.38) at 100 Hz, due to the increasing porosity and grain boundaries between the small sized grains. The low H_C and low dielectric loss between 100 and 100 kHz indicate its potential use as inductor and transformer for switch-mode power supplies [29]. MnCoFeO_4 NPs with the average particle size in the range of 30–40 nm synthesized via a simple one-pot co-precipitation method were also proven to be suitable as high-performance capacitors for electrical energy storage [73].

8. Conclusions and future perspectives

The Co ferrite continues to attract considerable attention due to its unique and exciting properties and opens new doors towards many potential applications. The properties of Co ferrite can be easily controlled by preparation technique, morphology, dopants type/content and cation distribution between tetrahedral (A) and octahedral (B) sites. There is a high number of studies that reported the physical, chemical, magnetic, electrical and optical properties of undoped and doped Co ferrites. Also, an increasing interest towards the incorporation of newer ions into the Co ferrite lattice in order to tailor its properties was noticed. The excellent properties of divalent transition metal doped Co ferrites, together with the possibility to tailor their particle size, shape, purity and chemical composition became a promising alternative for future generation nanomaterials designed for various industrial, environmental and medical applications.

Acknowledgements

This research was funded by the Romanian Research and Innovation Ministry, grant number 19PFE/2018. The APC was funded by the Romanian Research and Innovation Ministry, grant number 19PFE/2018 PROINSTITUTIO.

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