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Ferrimagnetism in cobalt ferrite ($CoFe_2O_4$) nanoparticles

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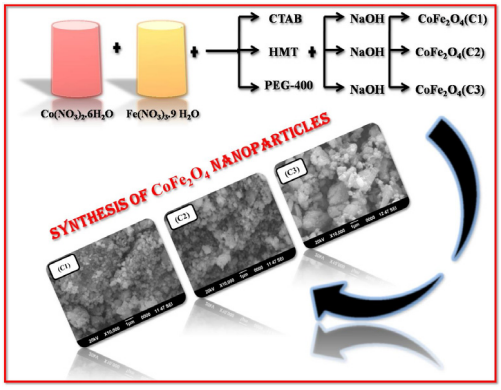
GRAPHICAL ABSTRACT



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ABSTRACT

Ferrimagnetic cobalt ferrite ($CoFe_2O_4$) nanoparticles were synthesized by employing co-precipitation method. Product physico-chemical and magnetic properties with respect to cetyl trimethylammonium bromide (CTAB), hexamethylenetetramine (HMT) and polyethylene glycol (PEG-400) surfactants were investigated. XRD pattern and Raman characteristic active modes revealed the cubic cobalt ferrite structure formation. SEM images explored spherical shaped product with different particle size. Identified strong PL emission peaks confirmed the product quality. IR metal oxygen vibration at 615 and 426 cm^{-1} revealed tetrahedral and octahedral site of cobalt ferrite system. Product electrochemical behavior was found to be size dependent and high specific capacitance was observed using CTAB. Room temperature ferrimagnetic behavior was confirmed through VSM studies. High saturation value as 66 emu/g was found using PEG. Particles with larger crystallite and particle size exhibited improved magnetic behavior.

1. Introduction

The ferrite physical and chemical properties grasp the researcher's interest to carry out research over a deep insight of analyzing the different ferrite magnetic, electric and opto-electric properties [1–5]. Nano-sized spinel ferrites have been focused due to its smaller particle size and narrow size distribution with larger surface area [1]. Nano-sized cobalt ferrite ($CoFe_2O_4$) filled up the major applications due to its unusual properties like magnetocrystalline high anisotropy ($1.8–3 \times 10^5$ J/m^3 at 300 K), good coercivity and enhanced magnetization [2]. Separately, cobalt

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oxide and iron oxide are also attracted for their unique properties and low cost [3,4]. Numerous techniques such as heat treatment, chemical substitution and sudden cooling etc. has been adopted to tune cobalt ferrite properties [5,6]. Generally, in bulk cobalt ferrite inverse spinel structure, Co^{2+} ions preferred octahedral B site and Fe^{3+} ions preferred tetrahedral A site of ferrite system. The cations distribution in ferrite system made the respective ferrite nanoparticles being significant in their unique properties for advanced applications. The ferrite magnetic property is directly depending on cations type and distribution in octahedral and tetrahedral sites and vice versa. The magnetic ferrite electron spins are arranged parallel within the crystal lattice site and anti-parallel between two sublattice sites whiles the net magnetization is the difference between two sites. The cobalt ferrite spinel structure is a hopeful phase material for magneto-sensitive systems [7], magnetic resonance imaging (MRI), tissue imaging and other environmental friendly applications [8]. Due to its high mechanical strength and wear anisotropy, it could be tied to the active materials in ferrofluids, microwave devices and adsorption applications [9]. The hierarchical, unusual and novel morphology nanoferrites such as nanoparticles, nanorods, nanocubes, nanobelt and nanoflowers help to adapt the corresponding material for future generation potential applications [10,11]. Several methods have been developed to synthesize nanoferrites including hydrothermal, sol–gel, ball milling, chemical reduction, microwave synthesis, mechanical alloying and co-precipitation etc. Among these methods, co-precipitation method has less toxic and fast and high yield synthesis method [12,13].

Gabal and his co-workers synthesized Zn-substituted $CoFe_2O_4$ via sucrose assisted combustion route and investigated the electromagnetic properties [14]. Pourgolmohammad and his team reported the effect of starting solution acidity on the characteristics of $CoFe_2O_4$ powders prepared by solution combustion synthesis method [15]. Fatemeh Shams and his research group statistically approached $CoFe_2O_4$ nanoparticles to optimize their characteristics using the response surface methodology [16]. Seema Joshi and her colleague worked on analyzing the effect of Gd^{3+} substitution on structural, magnetic, dielectric and optical properties of nanocrystalline $CoFe_2O_4$ [17]. Nagarajan Kannapiran and his group synthesized Poly(*o*-phenylenediamine)/$NiCoFe_2O_4$ nanocomposites and reported its characterization and the magneto-dielectric properties in details [18]. Mikio Kishimoto and his squad synthesized the FeCo particles through co-precipitation route using flux treatment for particle growth and examined the reduction property in hydrogen gas [19]. Kashif Ali and his coworkers synthesized $CuFe_2O_4/MnO_2$ nanocomposites for investigating its magnetic and dielectric properties successfully [20]. Bhowmik and Sinha jointly studied the improvement of room temperature electric polarization and ferrimagnetic properties of $Co_{1.25}Fe_{1.75}O_4$ ferrite by heat treatment [21]. Vijayasundaram and his team investigated chemically synthesized phase-pure nanoparticles and examine the role of influencing agents on the product purity [22]. Chaitali Dey and his research group reported the improved and efficient drug delivery system by hyperthermia treatment using magnetic cubic cobalt ferrite nanoparticles [23]. Chunming Yang and his team mates synthesized novel rare earth ions doped polyaniline/cobalt ferrite nanocomposites via a novel coordination-oxidative polymerization-hydrothermal route and investigated its microwave-absorbing properties [24]. In the present study, preparation of cobalt ferrite ($CoFe_2O_4$) nanoparticles employing simple co-precipitation route using different surfactants such as CTAB, HMT and PEG-400 has been explored. The surfactants effect on vital role in physico-chemical and magnetic properties of synthesized cobalt ferrite nanoparticles have been studied.

2. Materials and methods

Cobalt nitrate hexahydrate [$Co(NO_3)_2 \cdot 6H_2O$], ferric nitrate nonahydrate [$Fe(NO_3)_3 \cdot 9H_2O$], sodium hydroxide (NaOH), cetyl trimethylammonium bromide (CTAB), hexamethylenetetramine (HMT) and polyethylene glycol (PEG-400) were purchased from Sigma Aldrich. Wet chemical co-precipitation method was adapted to synthesize cobalt ferrite ($CoFe_2O_4$) nanoparticles. At first, 1 M (mol/L) $Co(NO_3)_2 \cdot 6H_2O$ and 2 M (mol/L) $Fe(NO_3)_3 \cdot 9H_2O$ were mixed together gradually under magnetic stirring and named as solution A. Then, 1 M (mol/L) CTAB was dissolved in 10 ml of deionized water and added slowly into the solution A. This solution was continued in stirring for about 10 min without any other disturbances and named as solution B. 20 M (mol/L) NaOH alkaline solution was poured into solution B as precipitating agent. The pale brown color solution was turned into dark brown color with particles indicated the successful reaction. The particles were washed with ethanol and water and centrifuged and dried at 100 °C overnight. The same procedure was followed by changing the surfactants as HMT and PEG-400. These dried powders were calcinated at 800 °C for 2 h and the final product was named as C1, C2 and C3 respectively and characterized comprehensively employing standard techniques. The product electrochemical behavior and the specific capacitance were examined by employing cyclic voltammeter (CV) study. The synthesized cobalt ferrite using various surfactants such as CTAB, HMT and PEG was chosen as active material. Initially 70% of active material, 20% of conducting agent (activated carbon) and 10% of binder (polyvinylidene hexafluoride-PVDF) were mixed together homogeneously with the help of N-methyl 2 pyrrolidinone solvent. This consistent mixture was layered on the low cost graphite sheet (1 × 1 cm) and dried in hot air oven for 14 h at 120 °C. Finally, the active material coated dried graphite sheet was adapted as working electrode in CV set-up. $Ag/AgCl_2$ was used as reference electrode, platinum wire was used as counter electrode and 1 M of NaOH was taken as electrolyte solution in the CV set-up of CH electrochemical workstation. By the formula and the area of CV curve, the specific capacitance value of respective material was calculated. The potential window was limited as −2.0 V to 1.0 V at various scan rates 15, 30, 45 and 60 respectively.

3. Results and discussion

Magnetic cobalt ferrite ($CoFe_2O_4$) nanoparticles are prolifically synthesized by employing wet chemical route with different surfactants such as CTAB, HMT and PEG-400 respectively. During synthesis, CTAB addition leads negative sides of precursor solution to move towards positive heads of CTAB and results lesser coalescence. The dissolved hexamine (HMT) in water produces continuous hydroxide (OH^-) ions to the precursor solution and abruptly changes the solution pH. The produced OH^- ions formed micelles layer around the cobalt ferrite hydroxide which leads to compact morphology of spherical shape products with lesser agglomeration. PEG-400 acted as a linking agent and yield larger size particles with uneven diameter and reveals sweeping change in the particle morphology. The advantages of synthesis methods in the present work for competitive products with other works reveals that one can synthesis highly dispersed and diverse morphology of cobalt ferrite nanoparticles when the influencing parameters such as CTAB, HMT and PEG-400 surfactant and the wet chemical synthesis conditions is optimized. The co-precipitation method is one of the simple, less toxic, fast, high yield and conventional methods without high cost to synthesis nanomaterials with desired controlled size assisted with different surfactants maintained at optimum condition. The efficiency of applications merely depend on the phase purity, crystallite size and particle size