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Auto Combustion Synthesis, Microstructural and Magnetic Characteristics of Nickel Ferrite Nanoparticles

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Abstract

Background/Objectives: Nickel ferrite nanoparticles are of great interest in various technical and medical applications, such as in sensors, biomedicine and catalysis. In the current investigation, $NiFe_2O_4$ nanoparticles have been successfully synthesized via the sol-gel self-ignited process using citric acid as fuel. **Methods/Statistical Analysis:** Self-ignited sol-gel process was adopted to prepare the sol with the addition of a suitable amount of ethanol. The sol was stirred at 80°C to achieve the dried gel. Thereafter, the dried gel was self-ignited through sol-gel method to reduce the metal iron and to attain the residual precursor. Finally, the residual precursor powder was sintered in air at 700°C for 4 hrs to obtained $NiFe_2O_4$ nanoparticles. XRD, FESEM, TEM, FTIR and XPS were used to characterize the synthesized products. **Findings:** The results confirm the formation of single phase spinel structure, identical grain size (~25 nm) and nodular particle morphology. Magnetic measurements indicated that nanocrystalline ferrite ($NiFe_2O_4$) nanoparticles are soft ferromagnetic in nature with high saturation magnetization 44.36 emu/g which is smaller than bulk one. **Applications/Improvements:** Self-ignited sol-gel method has salient advantages for the synthesis of novel ferrite nanoparticles (soft magnets) having improved performance well suited to drug delivery, magnetic resonance imaging and catalysis etc.

Keywords: $NiFe_2O_4$, Nanoparticles, Combustion Technique, Magnetic Property, XPS

1. Introduction

Magnetic nanocrystals, particularly those made of spinel ferrite with a composition of MFe_2O_4 (M=Ni, Mg, Mn, Zn, Cu, Co etc.), are feasibly vital materials due to their superior electrical and magnetic properties[1–3]. Spinel ferrites are attractive for a variety of possible applications in various important technological fields such as magnetic applications, biomedicine, and diverse catalytic process.

In most of the M-Ferrite systems, nickel ferrite-$NiFe_2O_4$ is a soft magnetic material with an inverse spinel structure. In this structure, Ni^{2+} ions present in B sites and Fe^{3+} ions distributed almost equally between the A and B sites[4]. The properties of nickel ferrite highly depend on the composition, morphology, and particle size which are strongly connected with the synthesis conditions. The $NiFe_2O_4$ nanoparticles have the characteristics that are anomalous properties to those of bulk materials properties.

There are several techniques to synthesize $NiFe_2O_4$ nanostructures including sol-gel[5,6], hydrothermal[7,8], co-precipitation[9], chemical route[10], ball milling[11], microwave assisted sol-gel method[12] and combustion methods[13-15].

Among the above available methods/routes, the self ignited sol-gel technique is a tremendous method to synthesize nanoparticles with maximum purity and good yield production. The self-combustion sol-gel process combines the combustion through chemical sol-gel process. Citric acid is commonly used as chelating agent. This process was successfully employed to produce different

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kinds of ferrites with homogeneous nanosized particles. It has the advantages such as using inexpensive precursors and reducing in consumption of external energy by usage of auto-combustion process[16].

Sol-gel combustion methods were distinguished by fast heating rates, high sintering temperatures and short reaction times. These features make combustion synthesis as an attractive method for the manufacture of useful materials at lower costs compared with conventional ceramic processes. Solution combustion synthesis has some other advantages: (a) low cost and simple equipment, (b) good stoichiometric control (c) low temperature process (d) formation of the desired products and (e) the nanoparticles synthesized through via sol-gel self combustion process have a good sintered-homogeneous composition[17].

In the present work, microstructural and magnetic characteristics of nickel ferrite synthesized via self-ignited sol-gel method using citric acid as fuel at a fairly low sintering temperature (700°C) was reported. XRD, FESEM, TEM, FTIR and XPS were used to characterize the nickel ferrite nanoparticles. The magnetism of nanoparticles was also investigated.

2. Materials and Methods

2.1 Preparation of $NiFe_2O_4$ Nanoparticles

The stoichiometric amounts of nickel nitrate and iron nitrate powders were mixed with a certain amount of deionized water to form homogeneous solution. The citric acid ($C_6H_8O_7H_2O$) as the complexing agent was then added to the metal nitrate solution with a molar ratio of 1:1. The chemical reaction was carried out in air without using any protective or inert gases. The pH of the solution was adjusted to about 9 by adding ammonia solution. Then, the mixed solution was poured into a dish and heated at 80°C stirring constantly to transform it into a brown gel. Being ignited, the dried gel burnt in a self propagating combustion way to form loose powder. The residual precursor was sintered in air at 700°C for 4 hours to obtain $NiFe_2O_4$ nanoparticles.

2.2 Characterization

The phase identification of obtained $NiFe_2O_4$ nanopowder was recorded for 2θ from 20° to 70° at a scan rate of 2° min^{-1} an using Brukar X-ray diffractometer with CuK_α radiation. The microstructure of the synthesized $NiFe_2O_4$ nanoparticles were characterized using a Field Emission Scanning Electron Microscopy (FE-SEM, Hitachi S-4800), at accelerating voltages of 15 kV, equipped with the energy dispersion X-ray spectroscopy (EDX) capabilities. The particle morphology of $NiFe_2O_4$ nanopowder was investigated by Transmission Electron Microscopy (TEM). FTIR spectrum was observed in the range of 400-4000 cm^{-1} at room temperature using Thermo Nicolet-6700 FTIR spectrophotometer. Magnetic properties were studied as a function of applied magnetic field (20 kOe) by using a commercial VSM - Physical Properties Measurement System (PPMS) Dynacool from Quantum Design. The electron binding energies for the nickel ferrite elements were measured by X-ray Photoelectron Spectroscopy (XPS) in a Perkin-Elmer PHI 1600 ESCA system.

3. Results and Discussions

The synthesis of ferrite nanoparticles was undertaken using metal nitrate precursors. Nanoparticles of nickel ferrite have been prepared by the citrate nitrate self-ignition route represented in a simple scheme in Figure 1(a). The chemical reaction as shown in Figure 1(b).

Figure 2a shows the XRD pattern of synthesized $NiFe_2O_4$. All the diffraction peaks matches well with the standard XRD pattern of $NiFe_2O_4$ (JCPDS card No.10-0325). The average crystalline size of the nickel ferrite nanoparticles, calculated using the Scherrer formula and is about ~23 nm.

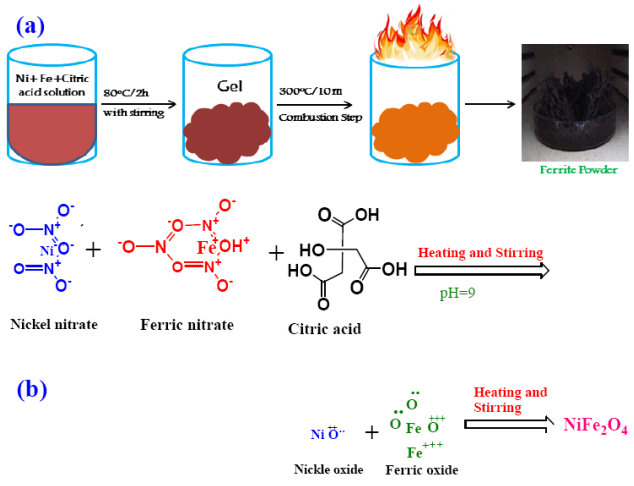

Figure 1. **(a)** Schematic diagram and **(b)** chemical reaction of $NiFe_2O_4$ nanoparticles synthesized by self-ignited sol-gel method.

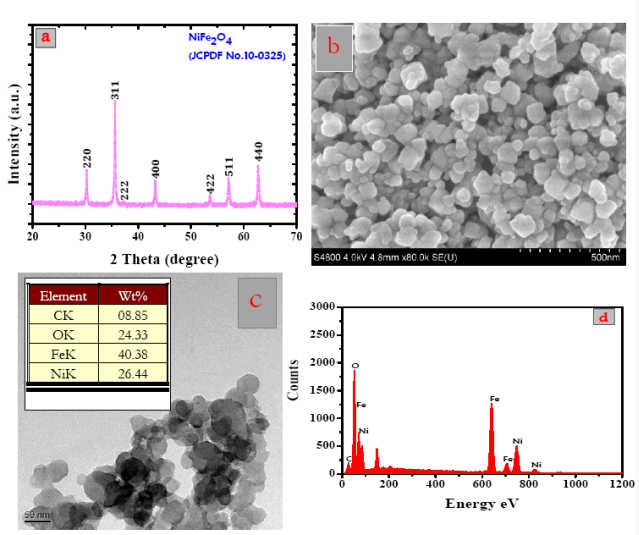

Figure 2. **(a)** XRD pattern, **(b)** SEM image, **(c)** TEM image and **(d)** EDX of $NiFe_2O_4$ nanoparticles.

The microstructure and morphology of the $NiFe_2O_4$ ferrite nanoparticles were investigated by FESEM and TEM (Figures 2b and 2c). Figure 2b reveals that the homogeneous microstructure of $NiFe_2O_4$ having grains size of ~26 nm. It is clearly visible form TEM bright-field image that the $NiFe_2O_4$ with particle sizes of 21–27 nm.

Energy dispersive X-ray (EDX) spectroscopy used for the elemental analysis of $NiFe_2O_4$ nanoparticles and as shown in Figure 2d. The EDX results confirmed that the synthesized $NiFe_2O_4$ does not contain any impurity.

The nickel ferrite nanoparticles were further examined with FTIR spectroscopy (Figure 3a). The vibrations at ~3423 cm^{-1} and 1633 cm^{-1} are attributed to the absorbed water molecules on the surface of the $NiFe_2O_4$ sample. The absorption band at 600 cm^{-1} assigned to stretching vibration of tetrahedral complexes and the band at 400 cm^{-1} is attributed to stretching vibration of octahedral complexes, which are indicative the formation of spinel ferrite structure[18]. The FTIR spectrum shows absorption band at 1380 cm^{-1} corresponding to NO^{3-} ions and the peak at ~1054 cm^{-1}. The peaks observed at 900-1050 cm^{-1} could be attributed to the C–O stretching due to adsorbed CO_2[19].

Magnetic studies of $NiFe_2O_4$ nanoparticles were measured at room temperature with the applied magnetic field of 20 KOe as shown in Figure 3b. The magnetic saturation value of 44.36 emu/g, which is lower than the theoretical value of 47.5 emu/g[20] reported in the literature. The lower values of magnetization may be due to small grain size effect of the ferrite nanoparticles. Smaller grains lead to larger surface to volume ratio. The ferrite nanoparticles have their core magnetic spins aligned ferromagnetically while on the surface spins are randomly inclined. Thus larger surface to volume ratio increases the surface spins entropy and magneto-crystalline anisotropy constant which consequently decreases the saturation magnetization. Similarly lower M_s Values are reported for Mn doped NiZn ferrite and Ca^{2+} doped Ni ferrite[21, 22].

XPS was used to analyze the elemental composition of the nickel ferrite nanoparticles. Figure 4 shows various regions (from 0 to 1100 eV) of the XPS spectra of $NiFe_2O_4$, confirming again the high purity of synthesized phase due to the presence of elements of iron, nickel and

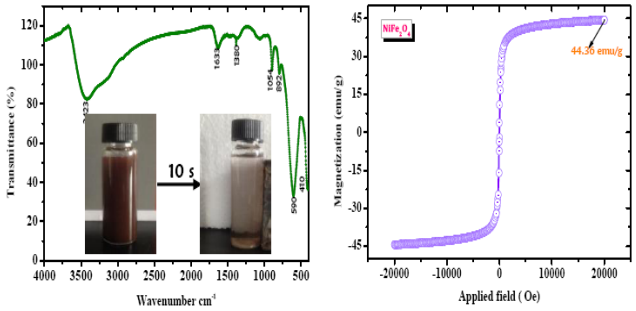

Figure 3. FTIR pattern (left) and M-H plot (right) of $NiFe_2O_4$ nanoparticles.

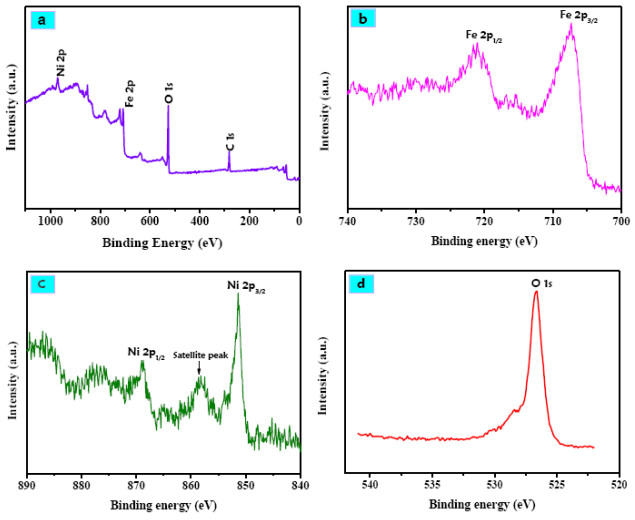

Figure 4. XPS spectra of NiFe2O4 nanoparticles: (a) wide spectrum, (b) Fe2p, (c) Ni 2p and (d) O 1s.

oxygen similar to EDX analysis. Figure 4(a) shows the wide range-scanning spectrum, which consists of Ni, Fe, and O and C components confirming formation of $NiFe_2O_4$ material. Figure 4b and d are the high-resolution XPS spectra of Fe 2p and O 1s obtained from $NiFe_2O_4$. In the Fe 2p spectrum (Figure 4(b)), the peaks at 707.4 eV and 721 eV ascribed to the $2p_{3/2}$ and $2p_{1/2}$ spin-orbit peaks, respectively. The peak with the binding energy of 707.4 eV is ascribed to the Fe^{3+} cation located at the octahedral site and 721 eV is attributed to the Fe^{2+} cation located at the tetrahedral site in the spinal structure. The binding energy values for Ni $2p_{3/2}$ and Ni $2p_{1/2}$ peak (Figure 4(c)) are 851.4 eV and 868.7 eV. The O 1s peak is observed (Figure. 4(d)), 526.7 eV, which corresponds to O2– ions of the pure materials. Both the valences and elemental characteristics were in fine concurrence with those in nickel ferrite composition.

4. Conclusion

In this study, the nanocrystalline nickel ferrite ($NiFe_2O_4$) was successfully synthesized through self-ignited sol-gel method. The XRD, XPS, FTIR and EDX analysis confirm the high purity, crystalline and spinel structure of synthesized phase ($NiFe_2O_4$). Magnetic measurements indicate that nanocrystalline ferrite ($NiFe_2O_4$) nanoparticles are soft ferromagnetic in nature with high saturation magnetization 44.36 emu/g which is lower than that of the bulk material. This result suggests their possible applications in drug delivery, soft magnets, magnetic resonance imaging, ferrofluids and higher frequency applications.

5. Acknowledgments

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