Synthesis of $NiFe_2O_4$ nanoparticles by organic surfactants-assisted sol-gel auto-combustion method, characterization and determination of band gap

Mahnaz Kamel Attar Kar [a], Faranak Manteghi [a*], Reza Fazaeli [b]

[a] Department of Chemistry, Iran University of Science and Technology, Tehran, Iran

[b] Department of Chemistry, Faculty of Sciences, South Tehran branch, Islamic Azad University, Tehran, Iran

Recently, nickel ferrite has attracted attention due to its multiple applications in storage devices, microwave devices, gas sensors, ferrofluids and catalysts. Nickel ferrites have excellent optical properties owing to their small band gap, which makes them suitable as a photocatalyst.
Among methods to synthesize nanocrystalline $NiFe_2O_4$, combustion method seems to be one of the facile and one step methods, since it allows the preparation of nanocrystalline $NiFe_2O_4$ with an equiaxial shape and narrow size distribution. Applying surfactants, which are composed from molecules along with sol–gel method can improve the properties of the synthesized powders.
In this present study, the sol–gel auto-combustion method is applied for synthesizing the $NiFe_2O_4$, $NiFe_2O_4$/CTAB and $NiFe_2O_4$/SDS nanocomposite, using nickel nitrate, iron nitrate, ammonia, citric acid and CTAB and SDS as surfactant. The nanoparticles were characterized by XRD, SEM, FT-IR and DRS. Powder XRD analysis and FT-IR spectroscopy confirmed formation of $NiFe_2O_4$ spinel phase. The particles size was estimated from SEM data. The energy band gaps were calculated by Kubelka-Munk model from UV–Vis absorption.

Keywords: $NiFe_2O_4$ nanoparticles, organic surfactant, sol-gel auto-combustion method, band gap

1. Introduction

Recently, nickel ferrite has attracted attention due to its multiple applications in storage devices, microwave devices, gas sensors, ferrofluids and catalysts. Nickel ferrites have excellent optical properties owing to their small band gap, which makes them suitable as a photocatalyst [1, 2]. It has inverse spinel structure. Spinel ferrite structure, which had a chemical formula of MFe_2O_4, is cubic with a close packed array of octahedral and tetrahedral metals. In the inverse spinel structure, the tetrahedral sites are occupied by Fe^{3+} ions and the octahedral sites are occupied by divalent metal ions (M^{2+}) and Fe^{3+} in equal proportions [3].
Various methods are used to synthesize ferrite nanoparticles, such as: combustion, mechano-chemical method, redox process, forced hydrolysis, co-precipitation, sol–gel, hydrothermal, polymer combustion method (PC), solid state method (SS), micro-emulsion, sonochemical, electrochemical and thermal decomposition method [4-12]. Among methods to synthesize nanocrystalline $NiFe_2O_4$, combustion method seems to be one of the facile and one step methods, since it allows the preparation of nanocrystalline $NiFe_2O_4$ with an equiaxial shape and narrow size distribution [13].
The incorporation of nanoscaled inorganic particles and organic materials (such as polymers) has been widely investigated, considering the extra advantages that could be obtained with combined properties of the inorganic materials (mechanical strength, magnetic and thermal

stability) and the organic polymers (flexibility, dielectric, ductility and processibility). Applying surfactants, which are composed from molecules, contains of hydrophilic head and hydrophobic tail, along with sol–gel method can improve the properties of the synthesized powders [14, 15].
In this present study, the sol–gel auto-combustion method is applied for synthesizing the $NiFe_2O_4$, NiFe2O4/CTAB and $NiFe_2O_4$/SDS nanocomposite, using nickel nitrate, iron nitrate, ammonia, citric acid and CTAB and SDS as surfactant.

2. Experimental

The starting materials for the synthesis of $NiFe_2O_4$, $NiFe_2O_4$/CTAB and $NiFe_2O_4$/SDS are $Ni(NO_3)_2{\cdot}6H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, ammonia (30%), citric acid monohydrate (98%) (CA), CTAB and SDS as surfactant. The required amount of metal nitrates and citric acid are taken so as to have a molar ratio of 1:1 and dissolved in 100 mL of deionized water. A required amount of ammonia is added into the solution in order to modify the pH value to about 7. The stoichiometric amount of surfactant was dissolved in minimum amount of water then added to the above solution. Dehydration of the solution was then done on a hotplate at 80◦C until a gel forms. Dry gels were heated in air to about 300◦C to invoke combustion. During combustion large amounts of gas were given off and a lightweight massive powder formed quickly. The resulting “precursor” powder was lightly ground by hand, as well as calcined at 800◦C for 2 h in a furnace to remove any organic rest [16, 17].

3. Results and discussion

3.1 XRD analysis

X-ray diffraction patterns of $NiFe_2O_4$, $NiFe_2O_4$ using CTAB as surfactant and $NiFe_2O_4$ using SDS as surfactant are shown in Figure 1. X-ray diffraction confirms the formation of single-phase (fcc) spinel structure for samples. The XRD pattern was compared and indexed using ICDD card no. (44–1485).

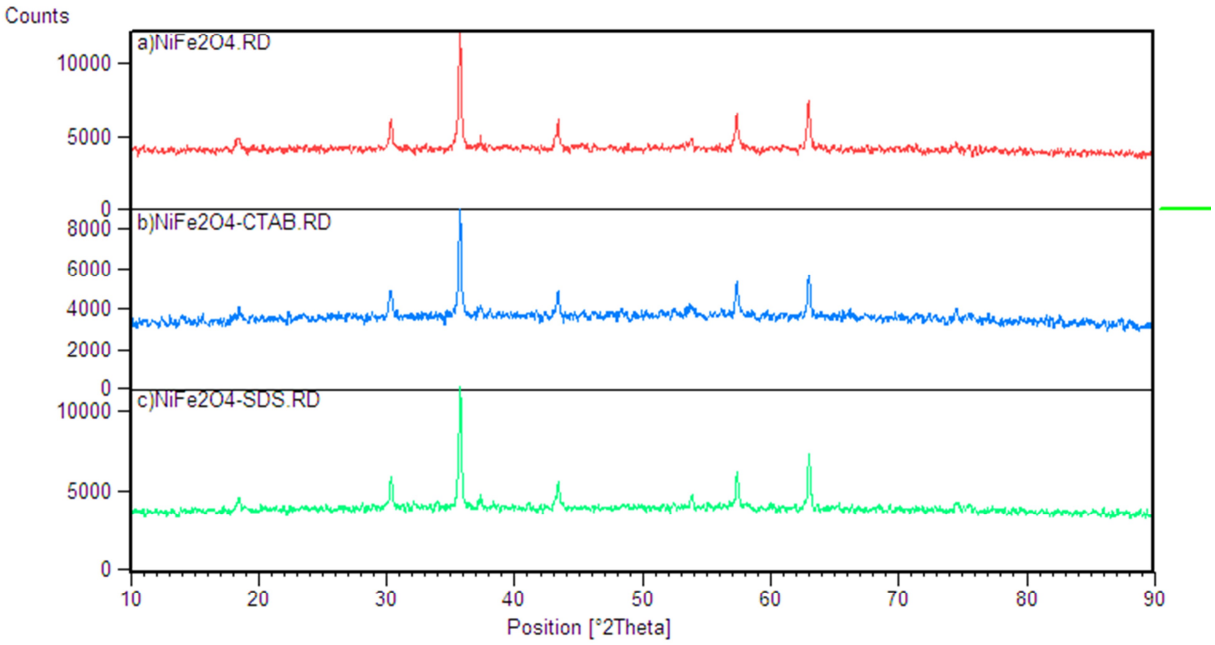

Fig. 1. XRD patterns: a) $NiFe_2O_4$, b) $NiFe_2O_4$/CTAB and c) $NiFe_2O_4$/SDS.

3.2 FT-IR analysis

Figure 2 shows the FT-IR spectrum of the $NiFe_2O_4$ powders. The characteristic peaks of tetrahedral and octahedral complexes could be observed at 588 cm^{-1} and 432 cm^{-1}. It is clear that the normal mode of vibration of tetrahedral cluster is higher and normal mode of vibration of octahedral cluster is shorter. The tetrahedral cluster has shorter bond lengths and the octahedral cluster has longer bond lengths [16].

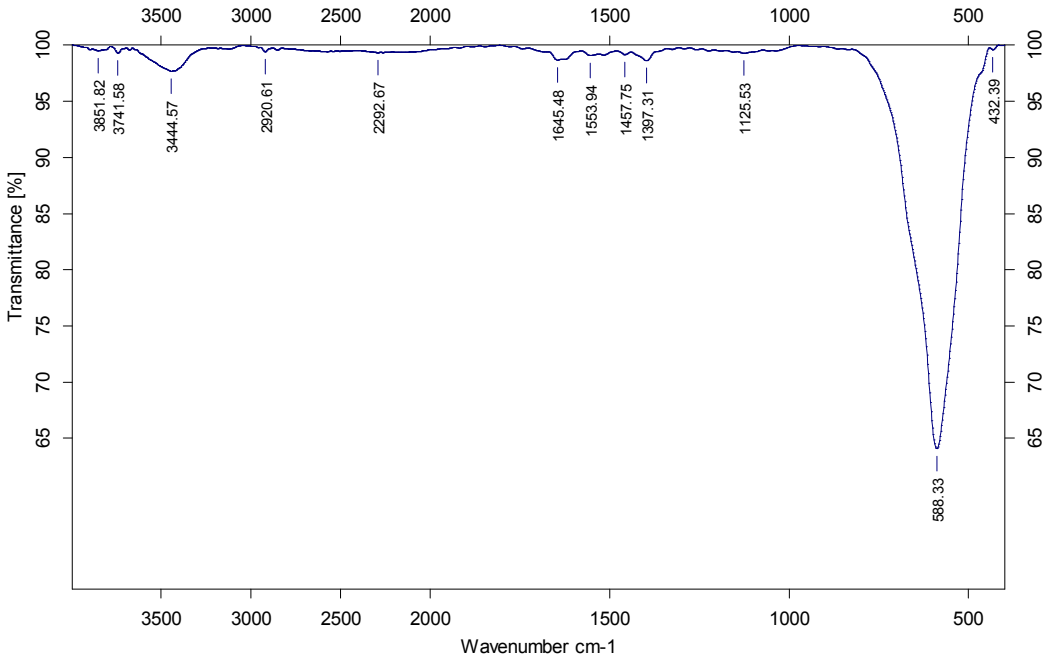

Fig. 2. FT-IR spectrum of nanoparticles of $NiFe_2O_4$ ferrite.

3.3 SEM analysis

The effect of surfactant on the morphology and size of the prepared samples have been studied. Figure 3 shows SEM images of samples prepared using CTAB and SDS as surfactant. The images showed completely agglomerated ferrite particles. It is clearly seen in the micrograph that the sample possess spherical nanosize grains. In comparison with other samples, it was observed that the nanoparticles are single crystal, roughly spherical and uniformly distributed.

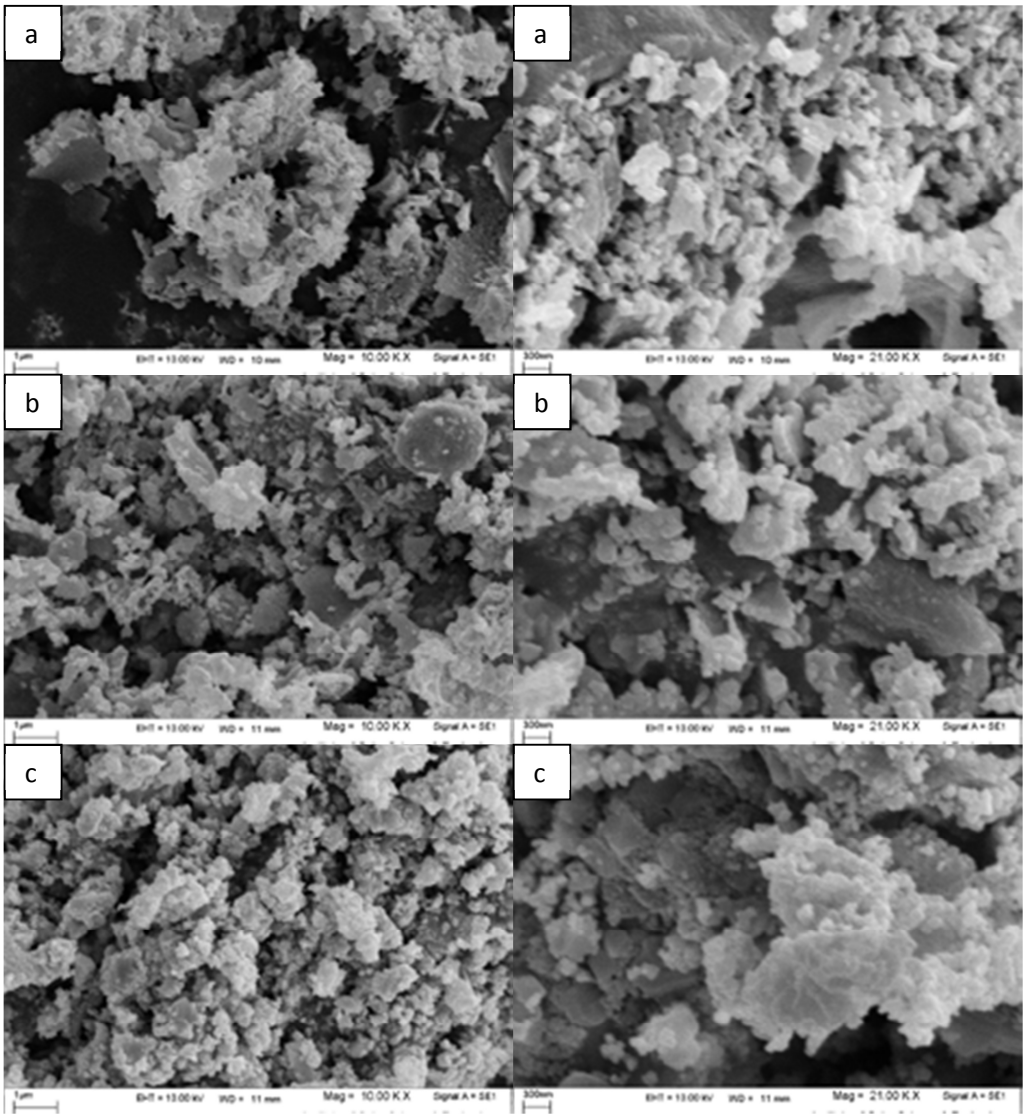

Fig. 3. SEM images of: a) $NiFe_2O_4$, b) $NiFe_2O_4$/CTAB and c) $NiFe_2O_4$/SDS.

3.4 DRS analysis

The analysis of optical absorption spectra is a powerful tool for understanding the band structure and band gap of both crystalline and noncrystalline materials. The optical properties of the ferrite samples were characterized by UV-DRS with the help of optical absorption data [18]. Optical band gap of nickel ferrite nanoparticles was estimated using the Kubelka-Munk relationship. The Kubelka–Munk plot $NiFe_2O_4$, $NiFe_2O_4$ using CTAB as surfactant and $NiFe_2O_4$ using SDS as surfactant has been presented in Figure 4. The calculated band-gap energies of $NiFe_2O_4$, $NiFe_2O_4$ using CTAB as surfactant and $NiFe_2O_4$ using SDS as surfactant were found to be 1.72, 1.77 and 1.77 eV, respectively.

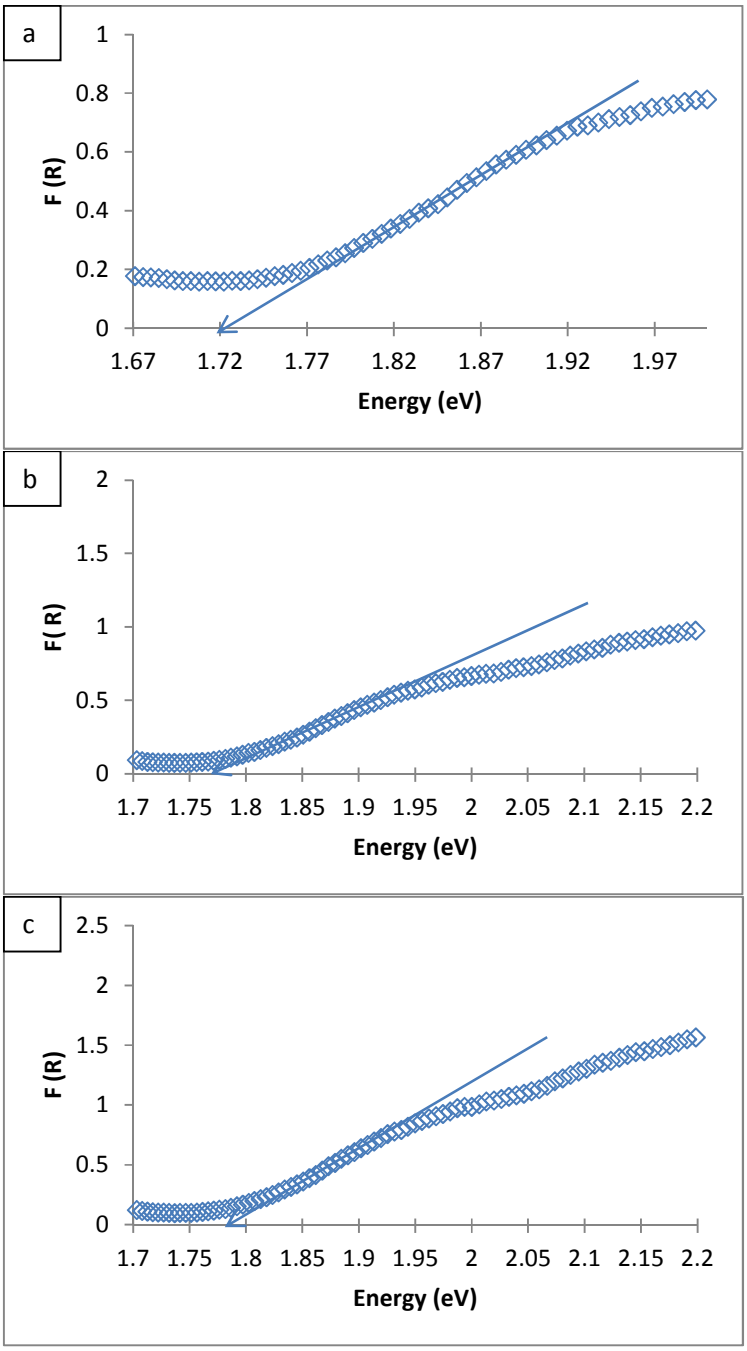

Fig. 4. The Kubelka–Munk plot for a) $NiFe_2O_4$, b) $NiFe_2O_4$/CTAB and c) $NiFe_2O_4$/SDS.

4. Conclusion

$NiFe_2O_4$, $NiFe_2O_4$/CTAB and $NiFe_2O_4$/SDS nanocomposite have been succesfully synthesized by sol-gel auto-combustion method. The nanoparticles were characterized by XRD, SEM, FT-IR and DRS. Powder XRD analysis and FT-IR spectroscopy confirmed formation of $NiFe_2O_4$ spinel phase. The particles size was estimated from SEM data. The energy band gaps were calculated by Kubelka-Munk model from UV–Vis absorption. Applying surfactants along with sol–gel method can improve the properties of the synthesized powders.

References

[1] P. Sivakumar, R. Ramesh, A. Ramanand, S. Ponnusamy and C. Muthamizhchelvan, Synthesis and characterization of $NiFe_2O_4$ nanosheet via polymer assisted co-precipitation method, Materials Letters, 65 (2011) 483–485.

[2] R. Tholkappiyan, K.Vishista, Combustion synthesis of Mg–Er ferrite nanoparticles: Cation distribution and structural, optical, and magnetic propertie, Materials Science in Semiconductor Processing, 40 (2015) 631–642.

[3] Y. Qi, Y. Yang, X. Zhao, X. Liu, P. Wu, F. Zhang and S. Xu, Controllable magnetic properties of cobalt ferrite particles derived from layered double hydroxide precursors, Particuology, 8 (2010) 207–211.

[4] M.S. Khandekar, R.C. Kambale, J.Y. Patil, Y.D. Kolekar and S.S. Suryavanshi, Effect of calcination temperature on the structural and electrical properties of cobalt ferrite synthesized by combustion method, Journal of Alloys and Compounds, 509 (2011) 1861–1865.

[5] P. Kumar, S.K. Sharma, M. Knobel and M. Singh, Effect of La^{3+} doping on the electric, dielectric and magnetic properties of cobalt ferrite processed by co-precipitation technique, Journal of Alloys and Compounds, 508 (2011) 115–118.

[6] Y.-D. Xu, G. Wu, H.-L. Su, M. Shi, G.-Y. Yu and L. Wang, Magnetoelectric $CoFe_2O_4$/Pb $(Zr_{0.53}Ti_{0.47})O_3$ composite thin films of 2-2type structure derived by a sol–gel process, Journal of Alloys and Compounds, 12 (2010) 112.

[7] J. Peng, M. Hojamberdiev, Y. Xu, B. Cao, J. Wang and H. Wu, Hydrothermal synthesis and magnetic properties of gadolinium-doped $CoFe_2O_4$ nanoparticles, Journal of Magnetism and Magnetic Materials, 323 (2011) 133–138.

[8] P. Chandramohan, M.P. Srinivasan, S. Velmurugan and S.V. Narasimhan, Cation distribution and particle size effect on Ramanspectrum of $CoFe_2O_4$, Journal of Solid State Chemistry, 184 (2011) 89–96.

[9] J.P. Vejpravova, V. Tyrpekl, S. Danis, D. Niznansky and V. Sechovsky, SSG or SFM state in $CoFe_2O_4$ nano-agglomerates fabricated by micro-emulsion method, Journal of Magnetism and Magnetic Materials, 322 (2010) 1872–1875.

[10] K. Kamal Senapati, C. Borgohain and P. Phukan, Synthesis of highly stable $CoFe_2O_4$ nanoparticles and their use as magnetically separable catalyst for Knoevenagel reaction in aqueous medium, Journal of Molecular Catalysis A: Chemical, 1381 (2011) 3–38.

[11] I.A. Amar, R. Lan, C.T.G. Petit, V. Arrighi and S. Tao, Electrochemical synthesis of ammonia based on a carbonate-oxide composite electrolyte, Solid State Ionics, 182 (2011) 133–138.

[12] B.Y. Song, Y. Eom and T.G. Lee, Removal and recovery of mercury from aqueous solution using magnetic silica nanocomposites, Applied Surface Science, 257 (2011) 4754–4759.

[13] M.S. Khandekar, R.C. Kambale, J.Y. Patil, Y.D. Kolekar, S.S. Suryavanshi, Calcination temperature on the structural and electrical properties of cobalt ferrite synthesized by combustion method, Journal of Alloys and Compounds, 509 (2011) 1861–1865.

[14] U. Kurtan, R.Topkaya, A.Baykal, M.S.Toprak, Temperature dependent magnetic properties of $CoFe_2O_4$/CTAB nanocomposite synthesized bysol–gel auto-combustion technique, Ceramics International, 39 (2013) 6551–6558.

[15] W.A.A. Bayoumy, Synthesis and characterization of nano-crystalline Zn-substituted Mg–Ni–Fe–Cr ferrites via surfactant-assisted route, Journal of Molecular Structure, 1056–1057 (2014) 285–291.

[16] A. Pradeep and G. Chandrasekaran, FTIR study of Ni, Cu and Zn substituted nano-particles of $MgFe_2O_4$, Materials Letters, 60 (2006) 371–374.
[17] N.J. Shirtcliffe, S. Thompson, E.S. O'Keefe, S. Appleton and C.C. Perry, Highly aluminium doped barium and strontium ferrite nanoparticles prepared by citrate auto-combustion synthesis, Materials Research Bulletin, 42 (2007) 281–287.
[18] R. Tholkappiyan, K. Vishista, Combustion synthesis of Mg–Er ferrite nanoparticles: Cation distribution and structural, optical, and magnetic properties, Materials Science in Semiconductor Processing, 40 (2015) 631–642.