

Super Capacitance study on Fe₃O₄ nanoparticles prepared by citrate assisted co-precipitation method

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Abstract

The main factual reason of this work deals with the synthesis and characterization of magnetite nanoparticles (Fe₃O₄) by a novel citrate assisted co-precipitation method. From TG/DT analysis (as-prepared sample) it shows that the calcination is essential for the formation of pure Fe₃O₄ nanoparticles. The synthesized powders were calcinated at 400 °C for three hours in air and were characterized by X-ray diffraction (XRD) which confirmed the formation of pure Fe₃O₄ nanoparticles. The surface morphology of ferrite oxide nanoparticles were analyzed through FESEM and FETEM which indicate that the particles are found crystalline and are in cubic shape. EDAX analysis exposed the presence of Fe and O. Zeta potential depicts the good stability of the prepared Fe₃O₄ nanoparticles. A good capacitance value of 183 Fg⁻¹ was observed for the scanning rate of 2mVs⁻¹ from the CV study exposes that the synthesized Fe₃O₄ nanoparticles can be used for super capacitor application.

1. Introduction

The materials that size ranges in nanoscale are of great importance in the areas of both fundamental and advanced research owing to their outstanding physical and chemical applications. In this ferrite nanoparticles have found much attractiveness because of their excellent electrical, magnetic, microwave devices, drug delivery systems and gas sensor [1-4]. Especially, nanoparticles of Fe₃O₄ found much attention in storage

application because in recent days energy shortages increase several fold. For which Fe₃O₄ based supercapacitor is an appropriate one [5]. Fe₃O₄ nanoparticles are very attractive in recent research works because of its higher electromagnetic performance, excellent chemical stability; mechanical hardness, high coercivity, and moderate saturation magnetization [6, 7]. Fe₃O₄ are of ferromagnetic in nature. The spinel structure of magnetite has the oxygen anions making face center closed packed structure with iron located at the interstitial and octahedral sites [8]. The nanoparticles can be synthesized by various wet chemical methods, like co-precipitation [9], hydrothermal [10], sol gel [11], micro-emulsion [12], thermal decomposition [13] and sono-chemical technique [14]. Apart from other type methods,

co-precipitation method has greater attraction because it can yield ultrafine, high purity and crystalline nanoparticles in very less duration [15-18]. In this paper we report the synthesis and characterization of Fe₃O₄ nanoparticles by using novel co-precipitation method by adding citric acid as a chelating agent.

2. Experiment and methods

For the synthesis of Fe₃O₄ nanoparticles by co-precipitation method [19] all the chemical reagents were bought from Merck chemicals (AR grade) of 99% pure and used without any additional purification. For which, 0.1M Fe (NO₃)₂·9H₂O and 0.29M of citric acid

($C_6H_8O_7 \cdot H_2O$) were dissolved in 20 ml of deionized water separately and were added respectively under constant stirring of 650 rpm. Appropriate amount of sodium hydroxide (NaOH) was added as precipitating agent to sustain a constant pH value around 9. Subsequently, the dissolved solution was stirred for 3h at 80 °C. Dark brown colour precipitate was formed and it was thoroughly washed several times with deionized water and acetone. Finally the precipitate was dried systematically in the oven to form the Fe_3O_4 powder at 100 °C for 2 hours and it was calcinated at different temperatures 400 °C, 600 °C and 800 °C.

Using PW3040/60 X'pert PRO powder X-ray diffractometer with $CuK\alpha$ radiation ($\lambda = 1.54060 \text{ \AA}$) at 40kV and 30mA the Crystalline phase of the Fe_3O_4 nanoparticles were identified. The step scans were recorded for 2θ values in the angular range from 10° to 80° through a scanning speed of 10^0 min^{-1} . By using Debye-Scherrer formula the average diameter of the crystals was calculated [20]

$$D = \frac{K \lambda}{\beta \cos \theta}$$

In which D is the crystallite size, K ($= 0.9$) is a constant associated to the shape of the crystal, λ is the wavelength of the radiation engaged, β is full width at half maximum (FWHM) of the attained characteristic peak in radians and θ is the Bragg diffraction angle. From the Joint Committee on Powder Diffraction Standards (JCPDS) database the phase identification was carried out. For studying the degradation behavior of the as-prepared sample, TG/DTA analysis was carried out with the help of instrument NETZSCH - STA 449 F3 JUPITER. FESEM with EDAX was recorded using a thermal emission scanning electron microscope, JSM6701F MODEL. Before examining, the samples were sputtered with gold. With the help of FETEM

instrument the morphology and size determination was accomplished using JEM 2100F. The selected area electron diffraction (SAED) patterns were confirmed by dispersing the sample over a carbon coated copper grid. The mean particle size and zeta potential are resolute using Dynamic light scattering (DLS) Zeta-sizer Nano ZS-90. An electrochemical property of the nano particles was examined by cyclic voltammetry (CV) model CHI 660.

3. Results and Discussion

3.1. X-ray Diffraction

The as-synthesized and calcinated samples were examined using XRD pattern which is shown in Fig.1.

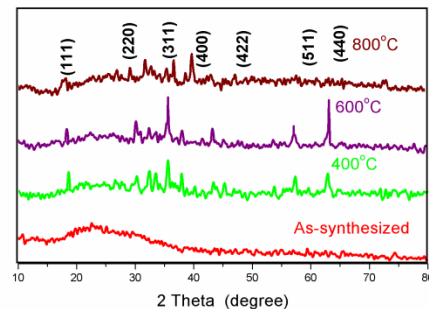


Fig.1 XRD Spectra of Fe_3O_4 nano particles as-synthesized and calcinated at different temperatures

For as-synthesized sample it doesn't show any peaks and specify that calcination is needed to stabilizing the particle size and preventing their agglomeration [21]. The XRD pattern of all calcinated samples exhibit the reflections with hkl values of (111), (220), (311), (400), (440), (422), (511) and (440) planes indicate the cubic phase with space group $Fd3m$ [22]. The attained XRD peaks are very well matched with the standard characteristics peaks of the cubic spinel lattice of Fe_3O_4 reported in JCPDS card no # 79 - 0417 [23]. The lattice parameter 'a' can be obtained by using the relation $a = d_{hkl} (h^2 + k^2 + l^2)^{1/2}$ and the value is found to be 8.390. The

obtained peak in the present study clearly indicates the development of pure Fe_3O_4 nanoparticle without any other external impurities. A similar result was reported by Ghandoores *et al.*, [23] for the preparation of Fe_3O_4 nanoparticles by co-precipitation method. The improved crystalline size with heat treatment is clearly indicating the essential of calcination also the as-prepared sample doesn't show any peak. From the Debye Scherer's formula the crystalline size were calculate for different calcination 400 °C, 600 °C and 800 °C and found to be 19 nm, 28nm and 36nm respectively. This result also show the particle size grows with increasing temperatures indicating the growth of Fe_3O_4 nanoparticles.

3.2 TG/DT analysis

Simultaneous thermo gravimetric analysis (TGA) and differential thermal (DTA) analysis of the as-prepared Fe_3O_4 was performed from room temperature to 850 °C. Fig. 2 represents the TGA and DTA curves of Fe_3O_4 nanoparticles.

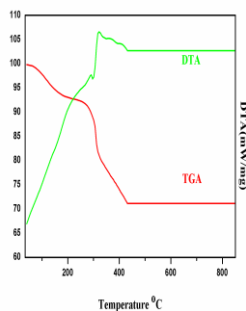


Fig. 2 TGA/DTA analysis of Fe_3O_4 nano particles

The decomposition of the chelating agent, citric acid, is predictable and happens in three major stages namely dehydration, decomposition of the anhydrous precursor and decomposition of organic precursors. A similar trend was reported by Catalano *et al.*, for the synthesis of Fe_3O_4 nanoparticles [24]. In which it was

clearly detected three major weight losses from the TG analysis in the range 35 °C to 850 °C. The first stage of weight loss is observed at a temperature below 97°C (3%) due to desorption of water. The next second stage weight loss is attained in the range from 97 °C to 290 °C (9 %) as a result of decomposition of organic templates. The final weight loss of (17%) is observed between 290°C and 410°C due to crystallization of the final product. No weight loss is found beyond 410°C representing the formation of pure Fe_3O_4 nanoparticles. The similar trend was clearly exposed by DTA where no change in peak beyond 410 °C confirms the formation of pure Fe_3O_4 nanoparticles.

3.3 Dynamic light scattering (DLS) and Zeta Potential

The size distribution (Zeta size) and the stability of the particle by zeta potential was studied for the Fe_3O_4 sample calcinated at 600 °C of pH 9 shown in Fig.3. From which in Fig.3 (a) depicts the Z-average value for the Fe_3O_4 nanoparticles as 227 nm. This greater size is owing to insolubility and aggregation of the sample in water.

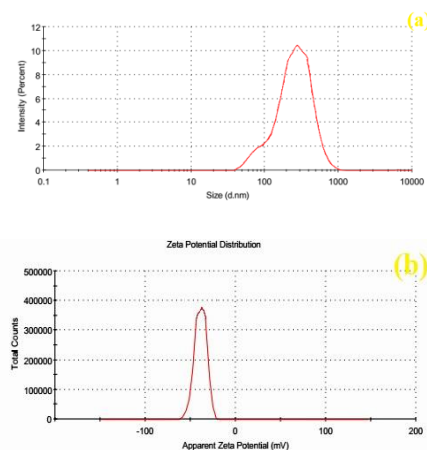


Fig.3 (a) Zeta sizer and Fig.3 (b) Zeta potntial of Fe₃O₄ nano particles calcinated at 600°C

Fig.3 (b) shows the result of the Zeta potential -31.3mV reveals the good stability of synthesized Fe₃O₄ nanoparticles. This result was in line with Catalano *et.al.*[24].

3.4 Field Emission Scanning Electron Microscope (FESEM) with EDAX

Fig. 4 (a), (b) and (c) represents the FESEM image of Fe₃O₄ sample calcinated at 600 °C. FESEM image reveals the cubic shape of Fe₃O₄ sample with some agglomeration.

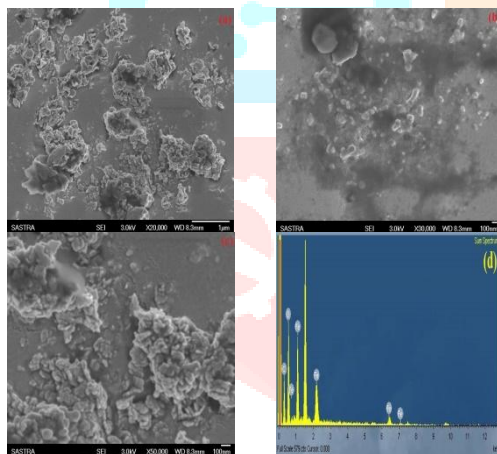


Fig.4 FESEM image of Fe₃O₄ nano particles calcinated at 600 °C with different magnifications (a), (b) and (c). Fig.3 and (d) Corresponding EDAX

This result is in line with Qing Liet.*al.*, for the preparation of Fe₃O₄ nanoparticles [25].EDAX analysis the reveals the chemical composition of the material it is shown in Fig. 4 (d) from which it was clearly observed that the synthesized material has only Fe and O. Also it clearly exposed that the synthesized sample is pure without any other impurities except the gold peak.The occurrence of gold peak is due to the thin coating on the

sample surface to make it conducting, which is essential to record the FESEM.

3.5 Field Emission Transmission Electron Microscope (FETEM) with SAED

The individual particles size, morphology and structure of Fe₃O₄ nanoparticles were easily visualized with the help of FETEM. Fig.5 (a) and (b) depicts the FETEM images of Fe₃O₄ nanoparticles calcinated at 600 °C. It confirms the detailed morphology of the sample and exposed its cubic nature. A similar result was reported by YunjiEomet.*al.*,for the preparation of Fe₃O₄ nanoparticles [26].The selected area electron diffraction (SAED) pattern of the cubic shaped Fe₃O₄ nanoparticles is shown in Fig.5 (c).

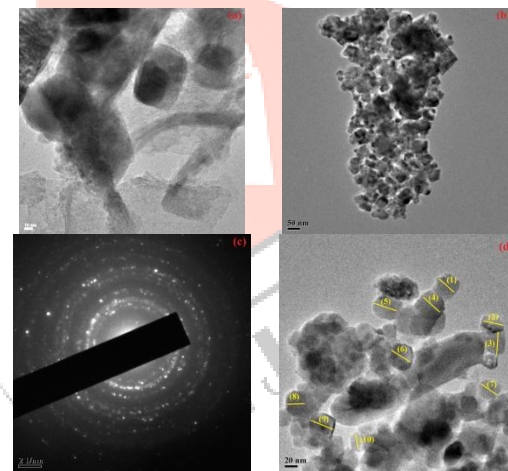
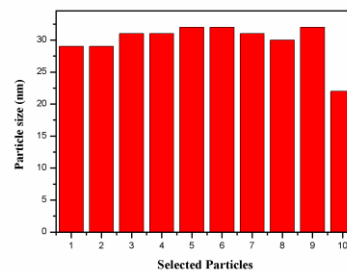


Fig.5 FETEM of Fe₃O₄ nano particles calcinated at 600 °C with different magnification (a) and (b); (c) Corresponding SAED; Fig.5 (d) Particle size measured using image j viewer software



Graph.1 Average Particle size using image j viewer software from FETEM

All spots are recognized as the diffractions from cubic Fe_3O_4 , which discloses the crystalline nature of NiFe_3O_4 nanostructure. With the help of “image j viewer” [27] software the individual particle size was calculated and it was shown in Fig. 5 (d) and graph 1; which is closely agree with the XRD result.

3.6 Cyclic Voltammetry (CV)

The CV curve of Fe_3O_4 electrode was noted at different scan rate of 2, 3, 5, 10, 20, 30, 50 and 100 mVs^{-1} were shown in Fig.6 (a). The shape of the CV curves is an ideal rectangular shape observed at 2mV s^{-1} . Further increasing the scan rate the observed pattern of the CV curve is transformed and it confirms the pseudo-capacitive nature of the material. The specific capacitances (SC) values of Fe_3O_4 electrode can be calculated by using the formula [28].

$$Cs = \frac{Q}{\Delta v \cdot m}$$

In which, Cs is the specific capacitance, Q the anodic and cathodic charges on each scanning, m is the mass of the electrode material (mg) and Δv is the scan rate (mVs^{-1}).

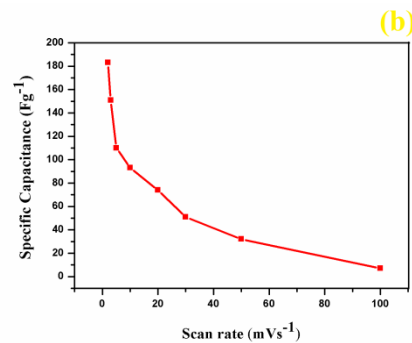
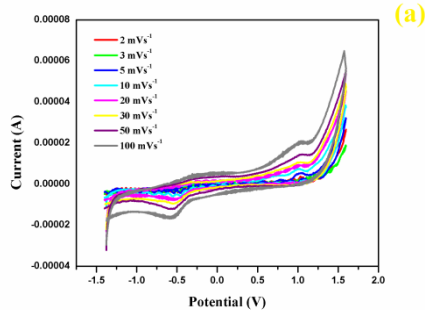


Fig. 6 (a) CV pattern of Fe_3O_4 nano particles calcinated at 600°C for different scan rates and Fig. (b) Different Scan rate and their Specific Capacitance values

Electrochemical measurements was done in 0.2 M tetra butyl ammonium perchlorate with a standard three electrode configuration containing of a sample (working electrode), an Ag/AgCl (reference electrode) and a high platinum wire (counter electrode)[29]. The scan rate is varied from 2mV s^{-1} to 100mVs^{-1} and its corresponding capacitance value decreased from 183 Fg^{-1} to 7 Fg^{-1} respectively is illustrated in Fig 6(b) and table 1.

| Fe_3O_4 (Calcinated at 600°C) | |
|--|--|
| Scan Rate(mVs^{-1}) | Specific Capacitance(Fg^{-1}) |
| 2 | 183 |
| 3 | 151 |
| 5 | 110 |
| 10 | 93 |
| 20 | 74 |
| 30 | 51 |
| 50 | 32 |
| 100 | 7 |

Table.1 shows the different scan rate and their specific capacitance value

From this it was clearly understandable that the lower specific capacitance values observed for higher scan rates indicate that the ionic diffusion takes place only for outer surfaces. A higher capacitance value of

183Fg^{-1} for the scan rate 2mV s^{-1} suggests that the prepared sample of Fe_3O_4 nanoparticles can be used as supercapacitor. In the present study the highest value 183Fg^{-1} was very much greater than that of the super capacitance reported by Jun Puet. *al.*, [30].

Conclusion

Fe_3O_4 nanoparticles were prepared by a simple high yielding and low-cost co-precipitation method. The structural, compositional and capacitive behaviors of the synthesized products were thoroughly studied. XRD study discloses the resultant product was Fe_3O_4 nanoparticles and the particle size got altered with the calcinated temperature. No weight loss was noticed from 410°C in TGA and the corresponding peak at 410°C in DTA study confirmed the formation of Fe_3O_4 . The FESEM and FETEM images confirmed that the particles were in cubic shape. EDAX confirmed the elemental composition of Fe_3O_4 nanoparticles were Fe and O without any other impurities. The particle size observed from FETEM analysis agrees very well with the particle size calculated from XRD. The zeta potential value exposed that the synthesized Fe_3O_4 nano particles have good stability. From CV study, higher capacitance value of 183Fg^{-1} was detected for Fe_3O_4 nanoparticles calcinated at 600°C recommended for super capacitance application.

References:

- [1] A.K. Boal and V.M. Rotello. 2004. Synthesis and Applications of Magnetic Nanoparticles in Nanoparticles: Building Blocks for Nanotechnology, Kluwer, New York, 2004, p. 1.
- [2] S. Sun, C.B. Murray, D. Weller, L. Folks and A. Moser. (2000). Monodisperse FePt nanoparticles and ferromagnetic FePt nanocrystal superlattices Science. 2000 Mar 17;287(5460):1989-92..
- [3] S. Sun, Adv. Mater. 18 (2006). Recent Advances in Chemical Synthesis, Self-Assembly, and Applications of FePt Nanoparticles. DOI: 10.1002/adma.200501464. pp.393–403
- [4] Q.A. Pankhurst, J. Connolly, S.K. Jones and J. Dobson. 2003. J. Phys. D Appl. Phys. 36 (2003) R167.
- [5] Guohong Li, Ruchun Li and Weijia Zhou. 2017. A Wire-Shaped Supercapacitor in Micrometer Size Based on Fe_3O_4 Nanosheet Arrays on Fe Wire. Nano-Micro Lett. (2017) 9:46 DOI 10.1007/s40820-017-0147-3
- [6] V. D. Nithya and N. SabariAru. 2016. Progress and development of Fe_3O_4 electrodes for supercapacitors. J. Mater. Chem. A, 2016, DOI: 10.1039/C6TA02582J.
- [7] H.E. Ghandoor, H. M. Zidan, Mostafa M.H. Khalil and M. I. M. Ismail. 2012. Synthesis and Some Physical Properties of Magnetite (Fe_3O_4) Nanoparticles. Int. J. Electrochem. Sci., 7 (2012) 5734 – 5745
- [8] N. D. Kandpal, N. Sah, R. Loshali, R. Joshi and J. Prasad. 2014. Co-precipitation method of synthesis and characterization of iron oxide nanoparticles. Journal of Scientific & Industrial Research Vol. 73, February 2014, pp. 87-90.
- [9] TaebinAhn, Jong Hun Kim, Hee-Man Yang, Jeong Woo Lee and Jong-Duk Kim. 2012. Formation Pathways of Magnetite Nanoparticles by Co-precipitation Method. J. Phys. Chem. C 2012, 116, 6069–6076. Doi:10.1021/jp211843g
- [10] T. Taniguchi, K. Nakagawa, T. Watanabe, N. Matsushita and M. J. Yoshimura. 2009. Hydrothermal Growth of Fatty Acid Stabilized Iron Oxide Nanocrystals. Phys. Chem. C 2009, 113, pp.839-843. DOI: 10.1021/jp8062433
- [11] A.S. Teja, and Koh. 2009. Synthesis, properties, and applications of magnetic iron oxidenanoparticles. Prog.Cryst.GrowthCharact.Mater. 2009, 55, 22–45.

- [12] J. Baier, J. Koetz, S. Kosmella, B. Tiersch, and H. J. Rehage. 2007. Polyelectrolyte-Modified Inverse Microemulsions and Their Use as Templates for the Formation of Magnetite Nanoparticles. *Phys. Chem. B* 2007, 111, 8612
- [13] J. Park, K. An, Y. Hwang, J. Park, H.J. Noh, J.Y. Kim, J. H. Park, N. M. Hwang, and T. Hyeon. 2004. Ultra-large-scale syntheses of monodisperse nanocrystals. *Nat. Mater.* 2004, 3, 891 DOI: 10.1038/nmat1251.
- [14] DavoodGhanbari, MasoudSalavati-Niasari and MajidGhasemi-Kooch. 2014. A sonochemical method for synthesis of Fe₃O₄ nanoparticles and thermal stable PVA-based magnetic nanocomposite. *Journal of Industrial and Engineering Chemistry*. Volume 20, Issue 6, 25 November 2014, Pages 3970-3974
- [15] D. Hu, Y. Wang and Q. Song. 2009. Weakly magnetic field-assisted synthesis of magnetite nanoparticles in oxidative co-precipitation. *Particuology* 2009, 7, 363–367.
- [16] A. Bandhu, S. Mukherjee, S. Acharya, S. Modak, S. K. Brahma, D. Das and P. K. Chakrabarti. 2009. Dynamic magnetic behavior and Mössbauer effect measurements of magnetite nanoparticles prepared by a new technique in the co-precipitation method. *Solid State Commun.* 2009, 149, 1790–1794.
- [17] B. Wang, Q. Wei and S. Qu. 2013. Synthesis and characterization of uniform and crystalline magnetite nanoparticles via oxidation-precipitation and modified co-precipitation methods. *Int. J. Electrochem. Sci.* 2013, 8, 3786–3793.
- [18] I. Nedkov, T. Merodiiska, L. Slavov, R. E. Vandenberghe, Y. Kusano, and J. Takada. 2006. Surfaceoxidation, size and shape of nano-sized magnetite obtained by coprecipitation. *J. Magn. Mater.* 2006, 300, 358–367.
- [19] Yan Wei, Bing Han, Xiaoyang Hu, Yuanhua Lin, Xinzhi Wang and Xuliang Deng. 2012. Synthesis of Fe₃O₄ nanoparticles and their magnetic properties. *Procedia Engineering* 27 (2012) 632 – 637. doi:10.1016/j.proeng.2011.12.498
- [20] MahmoudGoodarznaseri, Elias B. Saion, HosseinAbbastabarAhangar, MansorHashim, and Abdul HalimShaari. 2011. Simple preparation and characterization of nickel ferrite nanocrystals by a thermal treatment method. *Powder Technol.* 212, (2011) pp. 80–88
- [21] Maria Cristina Mascolo, Yongbing Pei and Terry A. Ring. 2013. Room Temperature Co-Precipitation Synthesis of Magnetite Nanoparticles in a Large pH Window with Different Bases. *Materials* 2013, 6, 5549-5567; doi:10.3390/ma6125549
- [22] M. Fonin, R. Pentcheva, Yu. S. Dedkov, M. Sperlich, D. V. Vyalikh, M. Scheffler, U. Rüdiger and G. Güntherodt. 2005. Surface electronic structure of the Fe₃O₄, 100...: Evidence of a half-metal to metal transition. *Physical Review B* 72, 104436 (2005).
- [23] H. E Ghandoor, H. M. Zidan, M. H. Mostafa Khalil and M. I. M. Ismail. 2012. Synthesis and Some Physical Properties of Magnetite (Fe₃O₄) Nanoparticles. *Int. J. Electrochem. Sci.*, 7 (2012) 5734 – 5745
- [24] E. Catalano and A. D. Benedetto. 2017. Characterization of physicochemical and colloidal properties of hydrogel chitosan-coated iron-oxide nanoparticles for cancer therapy. *IOP Conf. Series: Journal of Physics: Conf. Series* **841** (2017) 012010 doi:10.1088/1742-6596/841/1/012010
- [25] Qing Li, Christina W. Kartikowati, Shinji Horie, Takashi Ogi, Toru Iwaki and Kikuo Okuyama. 2017. Correlation between particle size/domain structure and magnetic properties of highly crystalline Fe₃O₄ nanoparticles. *Scientific Reports* volume 7, Article number: 9894 (2017) doi:10.1038/s41598-017-09897-5.
- [26] Yunji Eom, Mohamed Abbas, Hee Yoon Noh and Cheol Gi Kim. 2016. Morphology-controlled synthesis of highly crystalline Fe₃O₄ and CoFe₂O₄ nanoparticles using a facile thermal decomposition method. DOI:

10.1039/C5RA27649G (Paper) RSC Adv.,
2016, 6, 15861-15867.

- [27] B. Loganathan, V. L. Chandraboss, S. Senthilvelan and B. Karthikeyan. 2015. Surface enhanced vibrational spectroscopy and first-principles study of L-cysteine adsorption on noble trimetallic Au/Pt@Rh clusters. Phys. Chem. Chem. Phys. (2015)
doi:10.1039/c4cp05170j
- [28] K. Sathishkumar, N. Shanmugam, N. Kannadasan, S. Cholan and G. Viruthagiri. 2015. Opto, magnetic and electrochemical characterization of Ni_{1-x}Co_xO nanocrystals. J. Mater Sci. Mater electron. 26, 1881-1889 (2015)
- [29] P. Sivagurunathan and S.R. Gibin. 2016. J. Mater. Sci. Mater. Electron.(2016). Preparation and characterization of nanosized cobalt ferrite particles by co-precipitation method with citrate as chelating agent.doi:10.1007/s10854-016-4915-5
- [30] JunPu, Ling Shen, Shiyu Zhu, JieWang, Wu Zhang and ZhenghuaWang. 2014. Fe₃O₄@C core-shell microspheres: synthesis, characterization, and application as supercapacitor electrodes.J Solid State Electrochem (2014) 18:1067–1076 DOI 10.1007/s10008-013-2359-x

