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Solvothermal synthesis of porous Fe₃O₄ nanoparticles for humidity sensor application

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Abstract

In this research, the effect of PVP on magnetic properties and morphology of Fe₃O₄ nanoparticle (Fe₃O₄-NPs) is investigated. Also, the sensitivity of the humidity of the selected Fe₃O₄-NPs is studied. X-ray diffraction (XRD), transmission electron microscope (TEM), and vibration sample magnetometer (VSM) were used to characterize the synthesized Fe₃O₄-NPs. The XRD and TEM results demonstrated that Fe₃O₄-NPs were crystallized in cubic structure with spherical pores morphology. Superparamagnetic behavior was seen in the samples prepared with the maximum saturation of approximately 10 emu g⁻¹ for the sample synthesized using PVP:Fe(acac)₃ ratio equal to 4. The outcomes of the humidity sensing of the selected sample revealed that the prepared Fe₃O₄-NPs with a porous structure is a good candidate to be used for humidity sensing.

1. Introduction

Nowadays, magnetic nanostructures (MNPs) have been considerably regarded by the researchers because of their important features and applications. A number of of the magnetic nanostructures can be used in medical applications due to their non-toxicity and biocompatibility [1–3]. Several studies have been performed into the use of the materials in drug delivery [4, 5], magnetic resonance imaging (MRI) [6], hyperthermia [7, 8], medical diagnosis and therapy [9, 10] gas sensors [11–13], catalysts [14, 15], and environmental remediation [16, 17]. Several methods are used to synthesize magnetic material; e.g., sol-gel [18, 19], reverse micelle [20], co-precipitation process [21, 22], γ-ray irradiation [23, 24], non-aqueous route [25], microwave plasma synthesis [26], and hydrothermal treatment [27, 28]. Among these methods, solvothermal is a powerful technique to control the morphology and size of the nanostructure [29–34]. By this method, we can control the size, crystallinity, and the shape distribution of metal oxide nanostructures and synthesize well-crystallized and mono-dispersed ferrite nanostructures. In the solvothermal method, the morphology and size can be monitored by chemical parameters such as reaction time, surfactant, protective reactions, iron levels, etc. For example, Huang et al [35] produced Fe₃O₄ with a particle size between 450 and 750 nm by the solvothermal method and using NaAc·3H₂O as a surfactant. Also, Aiguo et al [36] synthesized Fe₃O₄ nanoparticles with particle size distribution of 15–190 nm using SDS and PEG as protective agents, using the solvothermal method and indicated that the magnetic properties of the magnetic material can be modified by controlling the synthesis conditions.

Iron oxide has different phase and component as (α, β, and γ)-Fe₂O₃ and Fe₃O₄. They have been widely used for sensing applications such as electrochemical sensors for glucose and dopamine detections. Also they were used for manufacturing gas sensors [37–42]. The humidity sensing of Fe₂O₃ nanoparticles was studied in the literature but we could not find any study for Fe₃O₄ nanoparticles [43].

In the present study, iron acetate (III), polyvinylpyrrolidone (PVP), and ethylene glycol were used respectively as a precursor, a size control polymer, and a solvent to prepare hollow Fe₃O₄ nanoparticles by solvothermal method. The Fe₃O₄-NPs were synthesized through different PVP:Fe(acac)₃ ratios and then characterized to study their magnetic properties and morphology. Also, the humidity sensing of the selected sample was studied.
2. Experimental

2.1. Materials
Iron acetate (III) (Fe(acac)₃, Merck, 99%) was used as a precursor. Polyvinyl-pyrrolidone (PVP) (Merck, 99%) and ethylene glycol (Mojalali) were used as a solvent. All the chemicals were utilized as ordered and without any preparation.

2.2. Synthesis of Fe₃O₄-NPs
The present research aims to study the effect of PVP:Fe(acac)₃ ratio on the morphology and size of Fe₃O₄-NPs. Therefore, three solutions were prepared with different PVP:Fe(acac)₃ ratios of 2, 4, and 6 that were named as samples (a), (b), and (c), respectively. To prepare these samples, first, 25 ml ethylene glycol was poured in a backer that is placed in an oil bath and the oil bath temperature was fixed at 60 °C. Next, 0.55 g Fe(acac)₃ was added to the ethylene glycol to obtain a red color solution. Then, a proper amount of PVP was added to the solution slowly. The mixed solution was left for 1 h and then the prepared solution was poured into a Teflon vessel supported by a stainless still autoclave. The autoclave was placed in an oven and the oven temperature was kept at 180 °C for 12 h. Deionized water using a centrifuge was used to wash the obtained dark brown precipitate.

![Figure 1. The prepared electrode pattern used for the sensing measurement.](image1)

![Figure 2. XRD patterns of the prepared Fe₃O₄-NPs by using (a) 1 gram PVP, (b) 2 grams PVP, and (c) 3 grams PVP.](image2)
three times. This process was replicated for the samples with the other amounts of PVP. Finally, the products were oven dried at 60 °C.

2.3. Sensor fabrication
RCA protocol was used for cleaning five Si-P silicon wafers (1 × 1 cm). The prepared samples dried properly using nitrogen gas. The S1813 photoresist was used for lithography technique to make electrode over the silicon surface. The photoresist was deposited on the silicon wafer using spin coater with a rotation speed of 2000 rpm during 30 s. The sample was baked in the oven at 110 °C for 30 min. After the UV light exposure through the inter-digit (IDT) mask (10 s, power 100%), the light affected parts of photoresist were removed by acetone and followed by electrode deposition. Chromium and gold deposited on the wafer with thicknesses of 20 nm and 100 nm respectively using thermal evaporation technique. The residual photoresistance was removed from the surface in the final stage to achieve IDT (see figure 1).

2.3.1. Setup
A semi-automatic set up used to measure the IDT sensor response to the humidity. The chamber consists of sensor stage, glass jar, a sensor holder, humidity meter, thermometer, heater, fan, electric part. Weston bridge circle and data logger were utilized to connect the sensors and to collect data, respectively. The water was evaporated using the heater and the humidity was controlled by controlling the volume of a water drop.

Figure 3. SSP plots of the prepared Fe₃O₄-NPs by using (a) 1 gram PVP, (b) 2 grams PVP, and (c) 3 grams PVP.
humidity sensor recorded the humidity during the measuring process (relative humidity of 10%–70%). Prova 803 and 6485 Keithley were utilized to read and record the resistance and current, respectively.

2.4. Characterizations
The structure of the prepared sample was studied by x-ray diffraction method (XRD, using Philips, Xpert, Cu Kα) and the obtained data were analyzed by Size Strain Plot (SSP) method. TEM, CM120, Philips was used for morphology observations. The magnetic properties of the Fe3O4-NPs prepared with the different amount of PVP were examined by Vibrating Sample Magnetometer, VSM (Magnetic Daghigh Kavir, MDKB, Iran).

3. Results

3.1. X-ray diffraction
Figure 2 shows the XRD patterns of the synthesized Fe3O4-NPs prepared by solvothermal methods. As mentioned earlier, different PVP:Fe(ac ac) ratios of 2, 4, and 6 were tested, which were named as samples (a), (b), and (c), respectively. Varying amounts all PVP were employed for fabrication of samples as (a) 1, (b) 2, and (c) 3 gr of PVP. The peaks at 2θ = 29.5°, 35°, 43°, 53°, 57°, 63°, 71°, and 74° are indexed to diffractions of (220) (311), (400), (422), (511), (440), (620), and (533) planes, respectively (PDF NO: 00-001-1111). Furthermore, it is
seen that the peak intensity of sample (b) is higher than that for the other samples, suggesting that this sample has better crystallinity than samples (a) and (c).

The samples’ crystallite size was determined by the SSP method through the g equation below:

$$(d_{hkl}/\beta_{hkl} \cos \theta)^2 = \frac{K}{D} (d_{hkl}^2/\beta_{hkl} \cos \theta) + \left( \frac{e}{2} \right)^2$$

where K for spherical particles ¼. The term $(d_{hkl}/\beta_{hkl} \cos \theta)^2$ is plotted against $(d_{hkl}^2/\beta_{hkl} \cos \theta)$ for the detected peaks of Fe3O4-NPs from $2\theta = 25^\circ$ to $2\theta = 75^\circ$. The slope of linearly fitted data estimated the particle size (figure 3) [44]. The crystallite size of samples (a), (b), and (c) were obtained to be 65 ± 2, 54 ± 2, and 54 ± 2 nm, respectively.

3.2. Magnetic properties

The magnetic properties of the prepared Fe3O4-NPs were studied by the vibrating samples magnetometer (VSM). Figure 4 presents the obtained results. All the samples show superparamagnetic behavior with the
saturation magnetizations obtained to be 6, 10, and 2 emu g\(^{-1}\) for the sample (a), (b), and (c), respectively. These results are smaller than that for (Ms = 100 emu g\(^{-1}\)). It is indicated that sample (b) indicates a higher saturation than samples (a) and (c), probably because of the better crystallinity of sample (b). This result is in good consistency with the XRD results.

3.3. TEM studies
Figure 5 presents the TEM micrograph of the prepared Fe\(_3\)O\(_4\)-NPs presented in. The results demonstrate that the morphology and size of the particles slightly affected by PVP quantity. The Fe\(_3\)O\(_4\)-NPs morphology was detected as spherical hollow shape for samples (a), (b), and (c) with a particle size of 86 ± 22, 81 ± 21, and 84 ± 28 nm, respectively.

3.4. Sensitivity measurement
The sensitivity, S, is measured as the differential in sensor resistance (Rs) in the chamber humidity environment and its resistance in the air humidity (Ra) as a function of humidity, equation (1).

\[
S = \left[ \frac{(R_a - R_s)}{R_s} \right] \times 100
\]

Fe\(_3\)O\(_4\) nanoparticles are porous and have oxygen atoms on the surface. These oxygen atoms arise due to the Fe\(_3\)O\(_4\) nanoparticles synthesis method. When humidity reaches to the surface and adsorbed by the nanoparticles, the resistivity of the samples decreased because of the charge carrier increased [45]. During the
adsorption of water by the surface, some of the hydrogen ions are dissociated and bounded with oxygen on the surface resulting to form the hydroxyl groups, equation (2) [46, 47].

\[ H^+ + O_{\text{surface}} \leftrightarrow [\text{OH}^-] \]  

(2)

The formed hydroxyl groups bound with the iron atoms of the lattice and free electrons are obtained, equation (3) [48].

\[ [\text{OH}^-] + \text{Fe} \leftrightarrow [\text{OH}^- \text{Fe}^3] + e^- \]  

(3)

These free electrons increase the conductivity of the samples.

Figure 6 presents the resistance variation of the sensor exposed to various humidity. Figure 7 indicates the humidity sensor sensitivity versus the room temperature humidity. As figure 7 shows, the association between the sensitivity and humidity has a linear behavior that can be fitted with a straight line using linear regression analysis. By applying the linear regression on the sensitivity-humidity curve, the slope of 0.508 with the coefficient of R² = 0.96 was obtained.

4. Conclusion

Fe₃O₄-NPs were synthesized by a solvothermal method using different PVP:Fe(ac ac)₃ ratios. The XRD results indicated cubic structure for the as-synthesized samples. The crystalline size of the samples (a), (b), and (c) was calculated by the SSP method and obtained to be 65 ± 2, 54 ± 2, and 54 ± 2 nm, respectively. The TEM micrograph demonstrated that the morphology of Fe₃O₄-NPs are hollow spherical with porous structure and size of 86 ± 12, 81 ± 21, and 84 ± 28 nm for samples (a), (b), and (c), respectively. Also, it was observed that the best size distribution is associated with sample (b). In addition, it was revealed that the Fe₃O₄-NPs properties were not much affected by the PVP:Fe(ac ac)₃ ratio; however, sample (b) shows the best results due to the higher saturation of the magnetization as 10 emu g⁻¹ than that of for sample (a) and (c). Therefore, the humidity-sensing test was conducted on sample (b). The result shows that Fe₃O₄-NPs (sample (b)) have a good response to humidity, making them appropriate for this application.

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Conflict of interest

There is no conflict of interest.

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References

[1] Bao Y, Wen T, Samia A C S, Khandhar A and Krishnan K M 2016 Magnetic nanoparticles: material engineering and emerging applications in lithography and biomedicine J. Mater. Sci. 51 513–53
[2] Canfaretta F and Piletsky S A 2014 Engineered magnetic nanoparticles for biomedical applications Adv. Healthcare Mater. 3 160–75
[3] Li X, Wei J, Aifantis K E, Fan Y, Feng Q, Cui F Z and Watari F 2016 Current investigations into magnetic nanoparticles for biomedical applications Journal of Biomedical Materials Research Part A 104 1285–96
[4] Mou X, Ali Z, Li S and He N 2015 Applications of magnetic nanoparticles in targeted drug delivery system J. Nanosci. Nanotechnol. 15 54–62
[5] Ulbrich K and Hola K I Suhr V, Bakandritis A, Tucek J and Zboril R 2016 Targeted drug delivery with polymers and magnetic nanoparticles: covalent and noncovalent approaches, release control, and clinical studies Chem. Rev. 116 5538–431
[6] Cheng K K, Chan P S, Fan S, Kwan S M, Yeung K L, Wang Y X J, Chow A H L, Wu E X and Baum L 2015 Curcumin-conjugated magnetic nanoparticles for detecting amyloid plaques in Alzheimer’s disease mice using magnetic resonance imaging (MRI) Biomaterials 44 155–72
[7] Hedayatnasab Z, Abnisa F and Daud W M A W 2017 Review on magnetic nanoparticles for magnetic nanofluid hyperthermia application Mater. Des. 123 174–96
[8] Obaidat I M, Issa B and Haik Y 2015 Magnetic properties of magnetic nanoparticles for efficient hyperthermia Nanomaterials 5 63–89
[9] Dilnawaz F and Sahoo S K 2015 Therapeutic approaches of magnetic nanoparticles for the central nervous system Drug Discovery Today 20 1256–64
Xu H, Shao M, Chen T, Zhuo S, Wen C and Peng M 2012 Magnetism-assisted assembled porous Fe₃O₄ nanoparticles and their gas sensor applications SENSORS ACTUATORS B 191 186–91

Matakatji D, Kolokoltsos E, Qureshi N, Mejia-Uriaire E and Saniger J 2013 A magmonic gas sensor based on magnetic nanoparticles NanoNanotech 7 9607–13

Guo X, Guo H, Wang Y, Li Y, Liu L, Li H, Lian H and Cheng Y 2018 Synthesis of novel H₂O₂–Fe₂O₃ porous nanotubes and their ultra-high acetone-sensing properties. J. Porous Mater. 25 1757–63

Govin J and Goriكو Y K 2014 Recent advances in the application of magnetic nanoparticle as a support for homogeneous catalysts Nanomaterials 4 222–41

Kainz Q M and Reiser O 2014 Polymer- and dendrimer-coated magnetic nanoparticles as versatile supports for catalysts, scavengers, and reagents. Acc. Chem. Res. 47 667–77

Elliott DJ W and Zhang W X 2001 Field assessment of nanoscale bimetallic particles for groundwater treatment Environmental Science & Technology 35 4922–6

Takafuji M, Ide S, Ishara H and Xu Z 2004 Preparation of poly(1-vinylimidazole)-grafted magnetic nanoparticles and their application for removal of metal ions Chem. Mater. 16 1977–83

Wang X, Zhang P, Gao J, Chen X and Yang H 2015 Facile synthesis and magnetic properties of Fe₃C/C nanoparticles via a sol–gel process Dyes Pigm. 112 305–10

Yadav R S, Havelica J, Hnatiuk M, Saigalik J, Alexander C, Palou M, Bartonikova E, Bohac M, Fakjorova F and Masilko J 2015 Magnetic properties of Co₀.₃Zn₀.₇Fe₃O₄ spinel ferrite nanoparticles synthesized by starch-assisted sol–gel auto combustion method and its ball milling J. Magn. Magn. Mater. 378 190–9

Gavrilovic T V, Jovanovic D I, Loipur V and Dramičanin M D 2014 Multifunctional Eu⁺- and Er³⁺-/Yb³⁺-doped GdVO₄ nanoparticles synthesized by reverse micelle method. Sci. Rep. 4 4209

Nikumbh A, Pawar R, Nighot D, Gujale G, Sangale M, Khanvilkar M and Nagawade A 2014 Structural, electrical, magnetic and dielectric properties of rare-earth substituted cobalt ferrites nanoparticles synthesized by the co-precipitation method J. Magn. Magn. Mater. 355 201–9

Safi R, Ghasemi A, Shoja-Razavi R, Ghasemi E and Sodace T 2016 Rietveld structure refinement, cations distribution and magnetic features of CoFe₂O₄ nanoparticles synthesized by co-precipitation, hydrothermal, and combustion methods Ceram. Int. 42 6375–82

Li H, Yang Z-Y, Liu C, Zeng Y-P, Hao Y-H, Gu Y, Wang W-D and Li R 2015 PEGylated ceria nanoparticles used for radioprotection on human liver cells under γ-ray irradiation Free Radical Biol. Med. 87 26–35

Raut A V, Jadhav S, Shengule D and Jadhav K 2016 Structural and magnetic characterization of 100-kGy Co₆₀ γ-ray-irradiated ZnFe₂O₄ NPs by XRD, W–H plot and ESR J. Sol-Gel Sci. Technol. 79 1–11

Pal M, Martinez Ayala A, Mathews N and Mathew X 2014 Synthesis and characterization of SnS nanoparticles through a non-aqueous chemical route for depositing photovoltaic absorber layers Journal of Nano Research, Trans Tech Publ 28 91–9

Szabo DV and Schlabach S 2014 Microwave synthesis of materials—from physics and chemistry to nanoparticles: A materials scientist’s viewpoint Inorganica 2 468–507

Ozel F, Kockar H and Karagaç O 2015 Growth of iron oxide nanoparticles by hydrothermal process: effect of reaction parameters on the nanoparticle size J. Supercond. Novel Magn. 28 823–9

Tadic M, Panjani M, Damjanovic V and Milosevic I 2014 Magnetic properties of hematite (α-Fe₂O₃) nanoparticles prepared by hydrothermal synthesis method Appl. Surf. Sci. 320 183–7

Ansari S, Kolekar Y and Sen D 2016 Investigations of structural and magnetic properties of cobalt ferrite magnetic nanoparticles synthesized by solvothermal chemical route Proc. of the Sixth DAE-BRNS Interdisciplinary Symp. on Materials Chemistry

Li S, Zhang T, Tang R, Qiu H, Wang C and Zhou Z 2015 Solvothermal synthesis and characterization of monodisperse superparamagnetic iron oxide nanoparticles J. Magn. Magn. Mater. 379 226–31

Nh S, Sun X, Li Y and Li C 2013 Solvothermal self-assembly of magnetic Fe₃O₄ nanochains by ethylenediamine functionalized nanoparticles for chromium (VI) removal J. Mater. Sci. 50 4270–9

Qi M, Zhang K, Li S, Wu J, Pham-Huy C, Diao X, Xiao D and He H 2016 Superparamagnetic Fe₃O₄ nanoparticles: synthesis by a solvothermal process and functionalization for a magnetic targeted curcumin delivery system New J. Chem. 40 4460–91

Shen M, Wu C, Lin C, Li C and Jia W 2014 Facile solvothermal synthesis of mesostructured chitosan-coated Fe₃O₄ nanoparticles and its further modification with folic acid for improving targeted drug delivery Nano 9 1450081

Zhao G, Wang J, Peng X, Li J, Yuan X and Ma Y 2014 Facile solvothermal synthesis of mesostructured Fe₃O₄/chitosan nanoparticles as delivery vehicles for pH-responsive drug delivery and magnetic resonance imaging contrast agents Chemistry—Asian Journal 9 546–53

Huang Y, Zhang L, Huan W, Liang X, Liu X and Yang Y 2010 A study on synthesis and properties of Fe₃O₄ nanoparticles by solvothermal method Glass Phys. Chem 36 325–31

Yan A, Liu Y, Qiu G, Wu H, Yi R, Zhang N and Xu J 2008 Solvothermal synthesis and characterization of size-controlled Fe₃O₄ nanoparticles J. Alloys Compd. 458 487–91

Qian G, Zheng H, Hong R, Deng S, Guo L, Hu R, Gao B, Huang M, Cheng L and Liu G 2014 Folic acid-conjugated Fe₃O₄ magnetic nanoparticles for hyperthermia and MRI in vitro and in vivo Appl. Surf. Sci. 307 224–33

Lee J, Mulmi S, Thangadurai V and Park S S 2015 Magnetically aligned iron oxide/gold nanoparticle–decorated carbon nanotube hybrid structure as a humidity sensor ACS Applied Materials & Interfaces 7 15306–13

Xu H, Shao M, Chen T, Zhou S, Wen C and Peng M 2012 Magnetism-assisted assembled porous Fe₂O₃ nanoparticles and their electrochemistry for dopamine sensing Microporous Mesoporous Mater. 153 35–40

Yu C J, Lin C Y, Liu C H, Cheng T L and Tseng W L 2010 Synthesis of poly (diallyldimethylammonium chloride)-coated Fe₃O₄ nanoparticles for colorimetric, sensing of glucose and selective extraction of thiol Bioens. Bioelectron. 26 913–7

Ghule B G, Shaitkh S F, Shinde M N, Sangale S S, Shinde P V and Mane R S 2018 Promoted room-temperature LPG gas sensor activities of graphene oxide@Fe₃O₄ composite sensor over individuals Mater. Res. Express 5 125001

Deshmukh V V and Patil A V 2018 Study of InO₂ and α-Fe₂O₃ nano-composite as a petrol vapor sensor Mater. Res. Express 5 625904

Esteban-Cubillo A, Tulliani J-M, Pecharramón C and Moya S J 2007 Iron-oxide nanoparticles supported on sepiolite as a novel humidity sensor J. Eur. Ceram. Soc. 27 1983–9

Khorsand Zak A, Yousefi R, Majid W H A and Muhamad M R 2012 Facile synthesis and X-ray peak broadening studies of Zn₁–xMgₓO nanoparticles Ceram. Int. 38 2059–64
[45] Liu X, Tao S and Shen Y 1997 Preparation and characterization of nanocrystalline $\alpha$-Fe$_2$O$_3$ by a sol–gel process Sensors Actuators B 40 161–5
[46] Muthurani S, Balaji M, Gautam S, Chae K H, Song J-H, Padiyan D P and Asokan K 2011 Magnetic and humidity-sensing properties of nanostructured Ca$_{x}$Co$_{1-x}$Fe$_2$O$_4$ synthesized via autocombustion J. Nanosci. Nanotechnol. 11 5850–5
[47] Suri K, Annapoorni S, Sarkar A and Tandon R 2002 Gas and humidity sensors based on iron oxide–polypyrrole nanocomposites Sensors Actuators B 81 277–82
[48] Arshaka K, Twomey K and Egan D 2002 A ceramic thick film humidity sensor based on MnZn ferrite Sensors 2 50–61