Synthesis and Characterization of Magnetite Nanoparticles and the Effect of \([\text{Fe(sac)}_2(\text{H}_2\text{O})_4].2\text{H}_2\text{O}\) complex on its magnetic properties

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Abstract

A novel inorganic complex (shell)@metal oxide (core) was demonstrated by simple and highly efficient synthesis of Fe$_3$O$_4$ nanoparticles (Fe$_3$O$_4$NPs) coated by \([\text{Fe(sac)}_2(\text{H}_2\text{O})_4].2\text{H}_2\text{O}\) complex through one-pot reaction of prepared Fe$_3$O$_4$ nanoparticles and \([\text{Fe(sac)}_2(\text{H}_2\text{O})_4].2\text{H}_2\text{O}\). The Fe$_3$O$_4$ NPs structure was characterized by infrared spectroscopy (IR), scanning electron microscope (SEM) and energy dispersive X-rays (EDX) while the resulted \([\text{Fe(sac)}_4(\text{H}_2\text{O})_2]@\text{Fe}_3\text{O}_4\)NPs was characterized using IR spectroscopy and XRD. The magnetic feature, which is one of physical properties of Fe$_3$O$_4$NPs and the newly synthesized core-shell \([\text{Fe(sac)}_2(\text{H}_2\text{O})_4]@\text{Fe}_3\text{O}_4\)NPs were examined in order to study how the Fe in its complex effects on the magnetic properties of magnetite nanoparticles.

Keywords: Inorganic complex@metal oxide, Fe$_3$O$_4$ NPs, \([\text{Fe(sac)}_2(\text{H}_2\text{O})_4].2\text{H}_2\text{O}\) complex, \([\text{Fe(sac)}_2(\text{H}_2\text{O})_4]@\text{Fe}_3\text{O}_4\)NPs, Magnetic properties.

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تحضير وتشخيص دقائق المغناتايت النانوية و تأثير المعقد على خصائصها المغناطيسية

[Fe(sac)_2(H_2O)_4].2H_2O

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المملصت

تم عرض اول معقد لاعضوي (قشر) على اوكسيد فنز (لب) بواسطة طريقة تحضير بسيطة وكمية عالية باستعمال دقائق Fe_3O_4 النانوية المغطاة بالمعقد [Fe(sac)_2(H_2O)_4].2H_2O اذ تم التفاعل ذو الدفعة الواحدة بين دقائق Fe_3O_4 والنانوية بواسطة مطيافية الاشعة تحت الحمراء ومجهر المسح الالكتروني وكذلك مطيافية تشتت الطاقة بالأشعة السينية بينما المركب الناتج دقائق [Fe(sac)_4(H_2O)_2]@Fe_3O_4 النانوية شخت باستعمال مطيافية الاشعة تحت الحمراء ومجهر الاشعة السينية. اختبرت الخصائص المغناطيسية والتي هي احدى الخواص الفيزيائية لكل من دقائق [Fe(sac)_4(H_2O)_2]@Fe_3O_4 و Fe_3O_4 النانوية من اجل دراسة كيف يؤثر الحديد في معقداته على الخواص المغناطيسية لدقائق المغناتايت النانوية.

الكلمات الدالة: معقد لاعضوي @اوكسيد فنز، دقائق Fe_3O_4 النانوية، المعقد [Fe(sac)_2(H_2O)_4].2H_2O، الخواص المغناطيسية، [Fe(sac)_2(H_2O)_4]@Fe_3O_4 NPs

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1. Introduction:

The nano structure of Fe$_3$O$_4$ with diameters (x,y,z) ranging from 1 and 100 nm and find an important nano material because it plays a main role in various fields as it was used as an adsorbent in micro solid phase extraction of metals or dyes [1, 2], data storage [3], biosensing [4] and drug delivery [5]. Magnetite nanoparticles (Fe$_3$O$_4$) can generally be separated from its reaction vessel by an external magnet such as neodymium magnet [6]. In recent times, the production of core–shell nanocomposites which may possibly be used as a catalysts for catalyzing organic reactions has been not far described [7]. Core–shell nanoparticles having a paramagnetic central material (core) such as iron or iron oxide are air and thermally stable and can be simply separated by an external magnet to evade old-style filtration methods [8]. Meanwhile, saccharin as an fake sweetener, the coordination chemistry of this heterocyclic amide have been extensively studied over the past 38 years [9]. There has been an important attention in the chemistry of metal ions bounded saccharine ligand over the past two decades ever since its demonstrations a varied kind of metal ion bonding fashions, and it is possibly useful as co-ligand in bioactivity studies. This ligand showed a variety of coordination modes to metals and was able to bind in a monodentate mode through either nitrogen atom via covalent bond, negatively charged or through the oxygen atom of carbonyl group. Furthermore, saccharine ligand has the ability to coordinate in a bidentate or even polydentate fashions with the contribution of the N- and O- donor atoms [9]. Saccharinate behaves as a monodentate ligand coordinates to the first row divalent metal ions through its deprotonated nitrogen atom [9-15]. In the present work, we report the preparation and characterization of inorganic core-shell nanoparticle containing [Fe(sac)$_2$(H$_2$O)$_4$].2H$_2$O as a shell and Fe$_3$O$_4$ nanoparticles as a core. Additionally, we report the magnetism properties of as-prepared inorganic core-shell nanoparticle.

2. Materials and Methods:

The chemicals used in this work were obtained from Sigma Aldrich and Merck and used without further purification. FT-IR spectra were recorded in the range 400–4000 cm$^{-1}$ with a Shimadzu 8400S spectrometer. The nanostructure of Fe$_3$O$_4$NPs was characterized using a Philips Xpert X-ray powder diffraction diffractometer (Cu K$_\alpha$, radiation, $\lambda$ = 1.54056 Å), at a scanning speed of 2°/min with 2$\theta$ ranging 10° to 80°. A thermal method using ultrasonic equipment with probe (6mm) model UP200ht was used for homogenizing of the mixture. The
morphology of Fe₃O₄ was obtained using Oxford instruments (FESEM) Tech, scanning electron microscope. Magnetic properties of the prepared nanoparticles were recorded with a vibrating-sample magnetometer model VSM, PPMS-9T.

2.1 Preparation of Fe₃O₄ Nanoparticles:

Fe₃O₄NPs were prepared by chemical co-precipitation. A solution of ferrous chloride tetra hydrate (FeCl₂·4H₂O) (2.58 g, 12.97 mmol), was added to an aqueous solution of ferric chloride hexahydrate (FeCl₃·6H₂O) (7.20 g, 26.63 mmol). The resulting solution was stirred for 4 hours at 80 °C, under nitrogen. Thereafter, 25% ammonium hydroxide solution (15 ml) was inserted drop wise into the resulted mixture, under vigorous stirring. The mixture was stirred at room temperature for further 3 hours. Subsequently, the resulted mixture left at room temperature to cool and the magnetite nanoparticles were decanted by magnetic decantation using neodymium magnet and then washed several times with distilled water until the pH of decanted solution equal 7.4. Fe₃O₄NPs was dried under vacuum at 75 °C. The resulting black powder of Fe₃O₄NPs (2 g, 67%) was dispersed in dry ethanol under ultrasonic irradiation for 1 hour to use in the next step [16].

2.2 Preparation of [Fe(sac)₂(H₂O)₄]·2H₂O

A solution of ferrous chloride tetra hydrate (0.2550g, 1.1317mmol) in distilled water (20 ml), was added to a solution of sodium saccharinate (0.4643g, 2.2631mmol) in distilled water (15ml), a brown precipitate was immediately formed. Moreover, the mixture was refluxed for 1 hour and the resulted powder was filtered, washed with hot water and dried at 60 °C for 12 hours. Brown solid. Yield: 0.5024 g (74%). Molar conductivity in DMSO (8.3 Ω⁻¹ cm⁻¹ mol⁻¹). IR (KBr, cm⁻¹): 3570vs υ(H₂O), 3099s υ(=C–H), 2953s υ(–C–H), 1622vs υ(C=O), 1577vs υ(C=C), 1464m υ(C=N), 1350vs, 1155vs υ(SO₂), 474m υ(M–N) [15].

2.3 Preparation of [Fe(sac)₂(H₂O)₄]@Fe₃O₄NPs

[Fe(sac)₂(H₂O)₄]@Fe₃O₄NPs were synthesized as follows. A mixture of an ethanolic solution of [Fe(sac)₂(H₂O)₄]·2H₂O (0.5103g, 1.000 mmol) in ethanol (50 ml) and Fe₃O₄NPs (0.5101 g, 2.203mmol) in ethanol (50 ml) was refluxed for 30 hours. After cooling, the brown precipitate was isolated magnetically, washed thoroughly with hot ethanol, and dried under vacuum.
3. Results and Discussion:

3.1 Preparation and Characterization of the Nanocatalyst

The core-shell \([\text{Fe(sac)}_2(\text{H}_2\text{O})_4]@\text{Fe}_3\text{O}_4\text{NPs}\) was synthesized according to the procedure shown in Scheme 1. In the beginning, \(\text{Fe}_3\text{O}_4\) NPs were synthesized through co-precipitation method by dissolving \(\text{FeCl}_2.4\text{H}_2\text{O}\) and \(\text{FeCl}_3.6\text{H}_2\text{O}\) and refluxing in the presence of ammonium hydroxide, thereafter, the addition of \([\text{Fe(sac)}_2(\text{H}_2\text{O})_4]\) complex in ethanol afforded the \([\text{Fe(sac)}_2(\text{H}_2\text{O})_4]@\text{Fe}_3\text{O}_4\text{NPs}\).

FTIR spectrum of \(\text{Fe}_3\text{O}_4\text{NPs}\) Fig. 1A, displays intense band at 588 cm\(^{-1}\) referring to the \(\nu(\text{Fe}_{\text{tetra-O}})\) of iron–oxygen at tetrahedral site. The two bands at 3433 and 1637 cm\(^{-1}\) correspond to the stretching and bending modes of hydroxyl group of water molecules, respectively, that adsorbed due to high surface area of the prepared \(\text{Fe}_3\text{O}_4\) NPs [18,19].

The particle morphology of the prepared \(\text{Fe}_3\text{O}_4\) NPs was categorized by SEM Fig. 2. The (SEM) result of the prepared \(\text{Fe}_3\text{O}_4\) NPs shows that the particle size were less than 40 nm with spheres-shaped in form. EDX of magnetite nanoparticle Fig. 3 shows oxygen and iron signals at 0.5 and 6.3, 0.6 keV of \(\text{Fe}_3\text{O}_4\) nano-particles. It also shows that the elemental ratio of Fe:O is 68:26% which is in agreement with the calculated ratio (72:27%).

FT–IR spectrum of \([\text{Fe(sac)}_2(\text{H}_2\text{O})_4]\).2\(\text{H}_2\text{O}\) shows a characteristic bands at 3570,1622 and 1464 cm\(^{-1}\) which corresponds to the stretching vibrations of (O–H, \(\text{H}_2\text{O}\)), C=O and C=N groups, while the two bands at 1350 and 1155 cm\(^{-1}\) attributes to the asymmetrical and symmetrical stretching vibration of \(\text{SO}_2\) group Fig. 1B. In the core-shell \([\text{Fe(sac)}_2(\text{H}_2\text{O})_4]@\text{Fe}_3\text{O}_4\text{NPs}\) spectrum, the absorptions of \([\text{Fe(sac)}_2(\text{H}_2\text{O})_4]\) are observed, along with a virtual broad band at 590 cm\(^{-1}\) assigned to the stretching vibration of the Fe–O group, indicating that the magnetic \(\text{Fe}_3\text{O}_4\text{NPs}\) are coated by \([\text{Fe(sac)}_2(\text{H}_2\text{O})_4]\) Fig. 1C. To confirm the presence of \(\text{Fe}_3\text{O}_4\) as a core, the structures of the newly prepared magnetic nanoparticles was characterized by (XRD), as shown in Fig. 4. There are six diffraction peaks at 20 about 30.11°, 35.50°, 43.21°, 53.03°, 57.13°, and 63.25° corresponding to the \((2\ 3\ 0)\), \((3\ 2\ 1)\), \((4\ 0\ 0)\), \((4\ 2\ 2)\), \((5\ 1\ 1)\), and \((4\ 5\ 0)\) planes [20] in the core-shell NPs, which is the standard pattern for crystalline magnetite with cubic structure. The diffraction pattern also shows diffraction peaks at 25.01°, 39.4°, 47.5° and 69.33° which attributed to the shell.
Scheme 1. Schematic diagram for preparing the inorganic core-shell

Fig. 1: IR spectra of (A): Fe₃O₄NPs, (B): [Fe(sac)₂(H₂O)₄].2H₂O and (C): [Fe(sac)₂(H₂O)₄]@ Fe₃O₄NPs.
Fig. 2: SEM of Fe$_3$O$_4$NPs.

Fig. 3: EDX of Fe$_3$O$_4$NPs.

Fig. 4: XRD pattern of [Fe(sac)$_2$(H$_2$O)$_4$]@Fe$_3$O$_4$NPs.
3.2 Magnetic Properties of the Nanoparticles:

The magnetometer can be used as a field calculating device by using a paramagnetic material. A vibrating sample magnetometer (VSM) depends on Faraday's law of induction, which informs that a changing magnetic field will produce an electric field. This electric field can be measured and provide us information about the changing magnetic field. The magnetization of Fe$_3$O$_4$ and [Fe(sac)$_2$(H$_2$O)$_4$]@Fe$_3$O$_4$NPs was measured and the results are shown in Fig. 5A-D. The results show an increase with an intensification in the magnetic fields and the saturated magnetization were 60.00 [21] and 39.96 emu g$^{-1}$ for Fe$_3$O$_4$ and [Fe(sac)$_2$(H$_2$O)$_4$]@Fe$_3$O$_4$NPs, respectively. The comparatively high VSM value indicates good superparamagnetism of Fe$_3$O$_4$NPs and [Fe(sac)$_2$(H$_2$O)$_4$]@Fe$_3$O$_4$NPs and the results show that the addition of ferrous-saccharine complex reduced the magnetism properties of the prepared Fe$_3$O$_4$ NPs.

![VSM of (a) Fe$_3$O$_4$ (b) [Fe(sac)$_2$(H$_2$O)$_4$]@Fe$_3$O$_4$NPs (c) well-dispersion of the [Fe(sac)$_2$(H$_2$O)$_4$]@Fe$_3$O$_4$NPs in water (d) isolation of the [Fe(sac)$_2$(H$_2$O)$_4$]@Fe$_3$O$_4$NPs by neodymium magnet.](image)

**Fig. 5:** VSM of (a) Fe$_3$O$_4$ (b) [Fe(sac)$_2$(H$_2$O)$_4$]@Fe$_3$O$_4$NPs (c) well-dispersion of the [Fe(sac)$_2$(H$_2$O)$_4$]@Fe$_3$O$_4$NPs in water (d) isolation of the [Fe(sac)$_2$(H$_2$O)$_4$]@Fe$_3$O$_4$NPs by neodymium magnet.

4. Conclusions:

In this study, the first inorganic core-shell nanoparticle that containing a complex of Fe(II) ion with saccharine ligand as a shell and Fe$_3$O$_4$ nanoparticles as a core has been successfully prepared and characterized. The yields of each step are high, and isolation of product from the
reaction mixture is so easy using out magnetic field. This novel nano core-shell has been used to study the magnetism properties and to make a comparison with the core material as a first attempt to determine the effect of complexes in the magnetic properties of chose iron oxide. The results show that the magnetic properties of Fe$_3$O$_4$NPs have been reduced after addition of a complex but the material still effected by magnetic field.

References

[1] Q. Zhou, Z. Zheng, J. Xiao, H. Fan, "Sensitive determination of As (III) and As (V) by magnetic solid phase extraction with Fe@ polyethyleneimine in combination with hydride generation atomic fluorescence spectrometry", Talanta, 156, 196 (2016).

[2] S. Li, Y. Gong, Y. Yang, C. He, L. Hu, L. Zhu and D. Shu, "Re recyclable CNTs/Fe$_3$O$_4$ magnetic nanocomposites as adsorbents to remove bisphenol A from water and their regeneration", Chemical Engineering Journal, 260, 231 (2015).

[3] G. Cordova, S. Attwood, R. Gaikwad, F. Gu, and Z. Leonenko, "Magnetic force microscopy characterization of superparamagnetic iron oxide nanoparticles (SPIONs) ", Nano Biomedicine Engineering, 6, 31 (2014).

[4] F. S. Hasany, H. N. Abdurahman, R.A. Sunarti and R. Jose "Magnetic iron oxide nanoparticles: chemical synthesis and applications review", Current nanoscience, 9(5), 561 (2013).

[5] J. Xie, and S. Jon, "Magnetic nanoparticle-based theranostics", Theranostics, 2(1), 122 (2012).

[6] R. Mrówczyński, A. Nan and J. Liebscher, "Magnetic nanoparticle-supported organocatalysts–an efficient way of recycling and reuse", Rsc Advances, 4(12), 5927 (2014).
[7] C. R. Ghosh and S. Paria, "Core/shell nanoparticles: classes, properties, synthesis mechanisms, characterization, and applications", Chemical reviews, 112(4), 2373 (2011).

[8] Z. Shokri, B. Zeynizadeh and S. A. Hosseini, "One-pot reductive-acetylation of nitroarenes with NaBH₄ catalyzed by separable core-shell Fe₃O₄@ Cu(OH)x nanoparticles", Journal of colloid and interface science, 485, 99 (2017).

[9] E. J. Baran and V. T. Yilmaz "Metal complexes of saccharin" Coordination chemistry reviews, 250(15-16), 1980 (2006).

[10] F. A. Cotton, L. R. Falvello, R. Llusar, E. Libby, C. A. Murillo and W. Schwotzer, "Synthesis and characterization of four vanadium (II) compounds, including vanadium (II) sulfate hexahydrate and vanadium (II) saccharinates", Inorganic Chemistry, 25, 3423 (1986).

[11] F. A. Cotton, E. Libby, C. A. Murillo, G. Valle, M. Bakir, D.R. Derringer, R. A. Walton, "Relatively Air-Stable M (II) saccharinates, M=V, or Cr", Inorganic Synthesis, 27, 306 (1990).

[12] F. A. Cotton, G. E. Lewis, C. A. Murillo, W. Schwotzer and G. Valle, "Comparative study of structures, including Jahn-Teller effects, in the saccharinate complexes, [M(C₇H₄NO₃S)₂(H₂O)₄].2H₂O, of chromium and zinc, as well as other divalent metal ions", Inorganic Chemistry, 23, 4038 (1984).

[13] F. A. Cotton, L. R. Falvello, C. A. Murillo and G. Valle "Single crystal x-ray study of solid solutions of a Jahn-Teller compound in an undistorted host: The Cr, Zn Saccharinate Hexahydrate System" Zeitschrift für anorganische und allgemeine Chemie, 540, 67 (1986).
[14] B. Kamenar, G. Jovanovski, and D. Gruden, "Two Ionic Saccharinates:(1a) Sodium Saccharinate 2/3 Hydrate, C_7H_4NO_3SNa. 2/3H_2O;(1b) Magnesium Disaccharinate Heptahydrate, (C_7H_4NO_3S) 2Mg. 7H_2O", Crystal Structure Communication, 11, 247 (1982).

[15] S. Z. Haider, K. M. A. Malik, K. J. Ahmed, G. B. Kauffman and M. Karbassi "Metal complexes of saccharin" Inorganic Synthesis, 23, 47 (1985).

[16] S. Z. Haider, K. M. A. Malik, K. J. Ahmed, H. Hess, H. Riffel and M. B. Hursthouse, "X-ray crystal structures of metal saccharin complexes of general formula \([M(C_7H_4NO_3S)_2(H_2O)_4].2H_2O\), where \(M=\) Fe(II), Co(II), Ni(II) and Cu(II)" , Inorganica Chimica Acta, 72, 21 (1983).

[17] R. Massart, "Preparation of aqueous magnetic liquids in alkaline and acidic media" IEEE transactions on magnetics, 17(2), 1247 (1981).

[18] R. M. Patil, P. B. Shete, N. D. Thorat, S. V. Otari, K. C. Barick, A. Prasad and S. H. Pawar, "Non-aqueous to aqueous phase transfer of oleic acid coated iron oxide nanoparticles for hyperthermia application", RSC Advances, 4, 4515 (2014).

[19] H. L. Fan, S. F. Zhou, G.S. Qi, Y.Z. Liu, "Continuous preparation of Fe_3O_4 nanoparticles using impinging stream-rotating packed bed reactor and magnetic property thereof", Journal of Alloys and Compounds, 662, 497 (2016).

[20] H. Nacimi, and S. Lahouti, "Magnetic nanoparticles coated with a chitosan anchored Schiff base complex of nickel (II) as an effective, reusable catalyst for one-pot synthesis of spirolactones", Transition Metal Chemistry, 43(3), 221 (2018).

[21] S. Su, B. Chen, M. He, B. Hu and Z. Xiao, "Environmental samples by ICP-MS after magnetic solid phase extraction with Fe_3O_4@ SiO_2@ polyaniline–graphene oxide composite", Talanta,119, 458 (2014).