Synthesis of α-Fe_2O_3 Nano Powders by Novel UV Irradiation Method

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Abstract

Alpha phase of iron oxide nanoparticles with different sizes from 10 to 45nm were synthesized by photolysis technique. Salicylaldehyde and amino phenol were used as started material to produce Schiff base which coordinate with iron metal to prepare complex. Nanoparticles were prepared by photolysis the ferric complex and calcined its salt. The result was showed reaction type oxidation-reaction due to transfer the charge from iron to ligand and convert ions for iron from +3 to +2. The irradiation system that used to prepare nanoparticles is 125 watts, ice bath was used to avoid high temperature and ensure happens photoreaction just. From the results, shift for C=N bond toward high frequency after irradiation was occur due to electronegativity of ferrous ions that product and the results from UV-visible technique obtained many type of transition for ligand and it complex at different wavelength. Energy gap for nanoparticles was determined by using UV-Vis while the morphology and average of nanoparticles were characterized by using AFM and TEM respectively. The identity of oxide was characterized by using XRD.

Key words: α–Fe_2O_3, Nano powder, Salicylaldehyde ($C_7H_6O_2$)α 2–amino phenol (C_6H_7NO), 125W lamp, Uv-irradiation.

تحضير الفا- اوكسيد الحديد النانوي بطريقة التشعيع بالاشعة الفوق البنفسجية

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الخلاصة

بواسطة تقنية التشعيع الضوئي، دقائق نانوية مع احجام مختلفة من 10 الى 45 نانومتر للطور الفا من اوكسيد الحديد المشخص بتقنية حيود الاشعة السينية قد حضرت. السالسالديهايد و 2- امينو فينول استخدمت كمواد اولية لإنتاج قاعدة الشيف التي تتناسق مع عنصر الحديد لتحضير المعقد. الدقائق النانوية حضرت من تشعيع المعقد ثم حرق الملح الناتج. النتائج اظهرت حدوث تفاعل من نوع اكسدة – اختزال بسبب انتقال الشحنة من الحديد الى الليكند وتحول الايونات من الحالة الثلاثية الى الثنائية. منظومة التشعيع التي استخدمت في تحضير الدقائق النانوية هي 125 واط، واستخدم حمام ثلجي لتجنب الارتفاع في درجة الحرارة وضمان حصول تفاعل ضوئي فقط. من النتائج التي تم التوصل اليها هو حدوث ازاحة في تردد اصرة شيف بين ذرتي الكاربون والنتروجين نحو الترددات العالية بسبب الكهروسلبية لايونات الحديدوز الناتجة والنتائج المستحصلة من تقنية الاشعة فوق البنفسجية – المرئية تظهر مجموعة من الانتقالات عائدة لليكند و معقده عند اطوال موجية مختلفة. وتم تعيين ثغرة الطاقة المحضورة للدقائق النانوية بواسطة تقنية الاشعة فوق البنفسجية – المرئية بينما تضاريس ومعدل الحجم النانوي تم تشخيصها بأستخدام تقنية مجهر القوة الذرية والمجهر الالكتروني النافذ على التوالي.

الكلمات المفتاحية: الفا – اوكسيد الحديد، نانو باودر، سالسالديهايد، 2- امينو فينول، مصباح 125 واط، اشعة فوق البنفسجية.

Introduction

Nanotechnology is understand and control of the material dimensions of approximately ranging from 1 to 100 nm and it interested in visualize, measure, and molding and processing materials at this range of size. The term nanotechnology was used as first time as 1974 and different about nano science term [1]. The properties of nano materials were differed from bulk materials due to surface area. The construction of nanomaterial was occurred in two ways: top to bottom and bottom to top. A nanomaterial was classified to one dimensional such as surface films, two dimensional as a fiber and three dimensional such as particles. The one of the important oxides are iron oxide nanoparticles that which has many forms such as α-Fe_2O_3, β-Fe_2O_3, γ-Fe_2O_3, ε-Fe_2O_3 and Fe_3O_4 and many implementations [2-8]. α-Fe_2O_3 is a common mineral and more stable phase of iron oxides [9]. Chemical precipitation, sol gel and hydrothermal methods were commonly used in the preparation of iron oxides. This research was converged on new method to prepare nano powder of α-Fe_2O_3 by using irradiation system of UV and it takes much advantage such as high purity of product, don't have temperature and economic. According these methods and during irradiation for complex, charge was transferred from metal to ligand and this causes for complex oxidation – reduction reaction.

Experimental

Without purification, chemical materials were used. The cell of immersion was showed in fig 1 and contains from 125W Hg lump (UV source), jacket for UV source in solution (quartz tube) and beaker was used as reactor. To avoid high temperature which results from UV source, the beaker was put in ice bath.

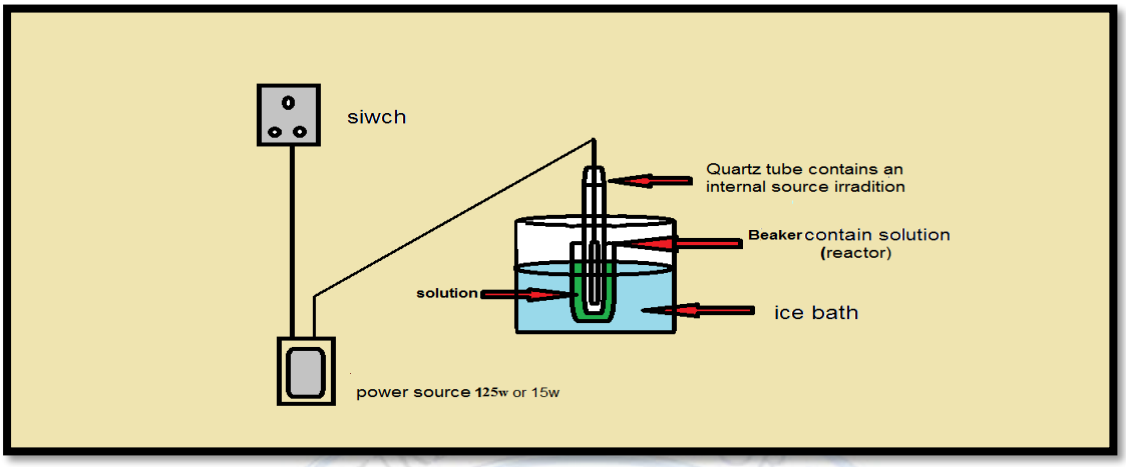


Figure 1: Photo irradiation system cell

Synthesis of α-Fe_2O_3 nanoparticles

(0.1) mole of Salicylaldehyde and (0.1) mole 2–amino phenol was mixed with them and dissolved in 40ml of ethanol in a 100ml beaker and stirred it until the precipitate appeared [10], then (0.008) mole of shiff base was mixed with (0.004) mole of $FeCl_3$ and dissolved in 20ml of ethanol then condensed the mixture for one hour. To make irradiate solution (0.002) mole of the iron complex was dissolved in 100ml of ethanol. A 100 ml of complex solution was irradiated for one hour when 125W lamp was used and green precipitate was formed, and then calcined precipitate at 200C to product brown precipitate without magnetic property formed.

Characterization

FTIR, UV-visible and quantitative metal analysis studies were used to confirm the synthesized complexes using [Fouror transform Infrared Spectrophotometer Shimadzu (Al-Mustansiriyah university), Spectrophotometer (Al-Mustansiriyah university) and Shimadzu Atomic Absorption /Flame Emission Spectrophotometer A.A 880 (ibn sina company)]. The surface image and average particle size of α-Fe_2O_3 was recorded by atomic force microscope (The Digital Instruments, Veeco Metrology Group SPM _AA 3000, AFM contact Mode, Angstrom, Advanced, Inc., 2008, USA) and Transition Electron microscope (JEOL JEM - 2100) at Baghdad and Mansoura university while the crystal system determination of α-Fe_2O_3

were characterized by XRD (Shimadzu-XRD-6000 with Nickel- copper filter) (Cu Kα, λ=1. 5406 A°) at ibn al haytham collage.

Result and Discussion

FTIR studies

The absorption of ligand was appeared at top fig 2, three peaks at 1630, 3049 and 3219 cm^{-1} assigned to (C=N) and (O-H) groups respectively and peak at 1274cm^{-1} belonging to (C-O) group but when compare the spectra of ligand with its complex at same fig, observed the shift in (C=N) group towards the frequency lower for 30cm^{-1} which shows the coordinate iron with nitrogen atoms and broadband located at 3271cm^{-1} was referred to the frequencies of (O-H) due to coordinate ligand by through the oxygen atom with iron. At same fig, showed shift in (C=N) group towards the frequency higher for 18cm^{-1} due to electronegativity for ferrous ion. Three bands located at 482, 534 and 568cm^{-1} associated to (Fe-N) and Fe-O respectively [11, 12].

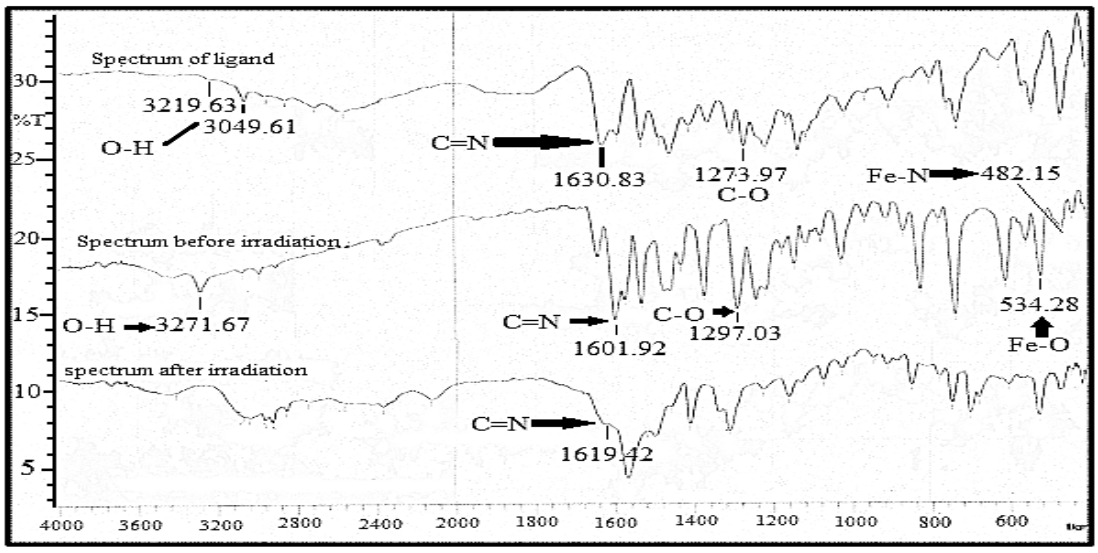
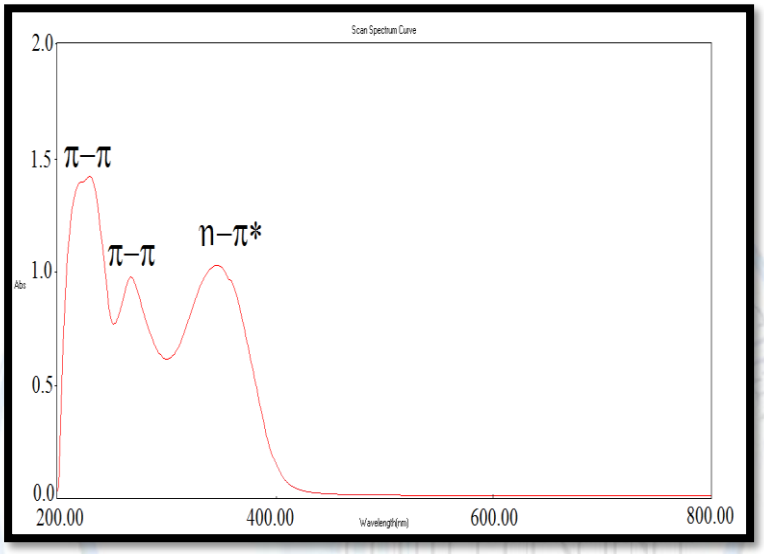


Figure 2: FTIR of ligand and complex before and after irradiation

UV- visible and synthetic formulas studies

Electronic spectra of the ligand and iron complex were studied by using DMSO as solvent in the wavelength (200-800 nm). The absorption spectrum of ligand was appeared bands at (230 and 268) nm back to transfer π-π* because of the existence of π bonds for banzine and

isothemine group and absorption band at 348nm back to transfer n-π*, fig (3) shown the spectrum of ligand whlie fig (4) shown the spectrum of complex the electronic spectra of the complex was appeared three types electronic, the first belong to ligand (π-π* and n-π*) at (205-219 and 332nm), the second type is charge transitions of a kind LMCT at (388nm) and the third type is weak transitions d-d transitation at(467nm) [13, 14] .



Figuer 3: uv-vis spectrum of ligand

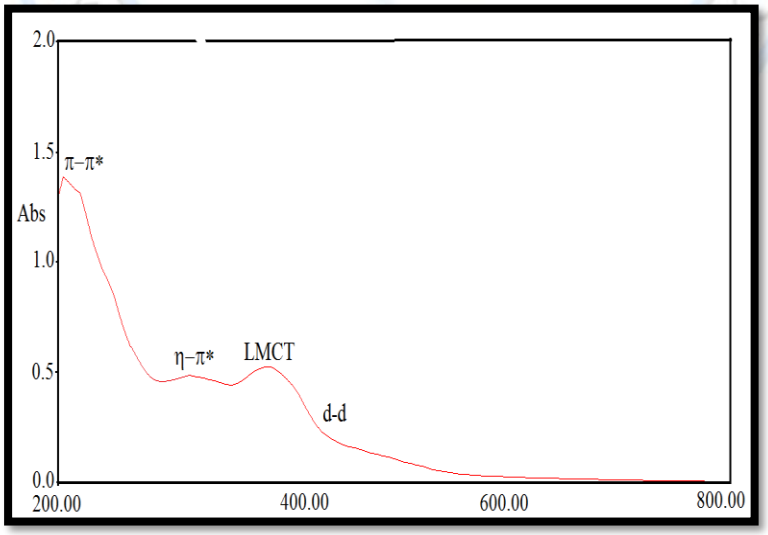


Figure 4: Uv-vis spectrum of iron complex

The energy gap (Eg) for hematite nanoparticles was determined by using UV-Vis for it by edge of absorption of nanoparticles from the formula:

$Eg = 1240/\lambda max$

Due to a quantum confinement effect [15], blue shift was showed mostly for nanoparticles and energy gap equal to 4.55eV.

The synthetic formulas for the complex have been proposed by using flame atomic absorption spectroscopy and the proposed formulas of the complex is:

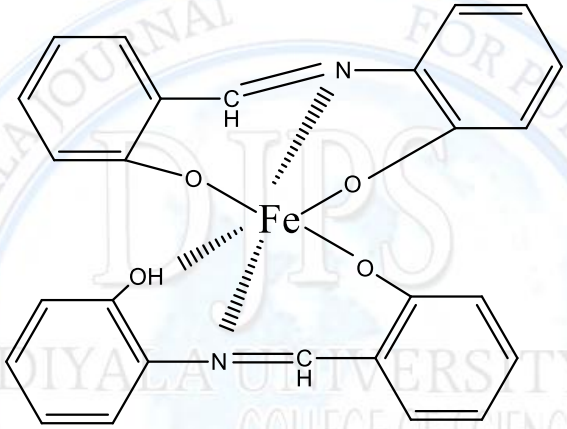


Figure 4: the proposed formulas of the complex

The mechanism of the photolysis method

The photolysis mechanism for prepare of the oxide can be suggest as follows:

$$Fe^{III}(L)_2 + h\upsilon \longrightarrow (Fe^{III}\,L)^{+1}L^{1-} \longrightarrow Fe^{II}\,L + L^{\cdot}$$

$$Fe^{II}\,L \longrightarrow \alpha\text{-}Fe_2O_3 + CO_2 + H_2O$$

AFM and TEM studies

For oxide prepared, the morphology of surface for it was showed by AFM and TEM at fig 5 and 6 respectively. Average diameter 28.54 nm with many agglomerations of particles in Nano scale and homogenous was obtained from chart.

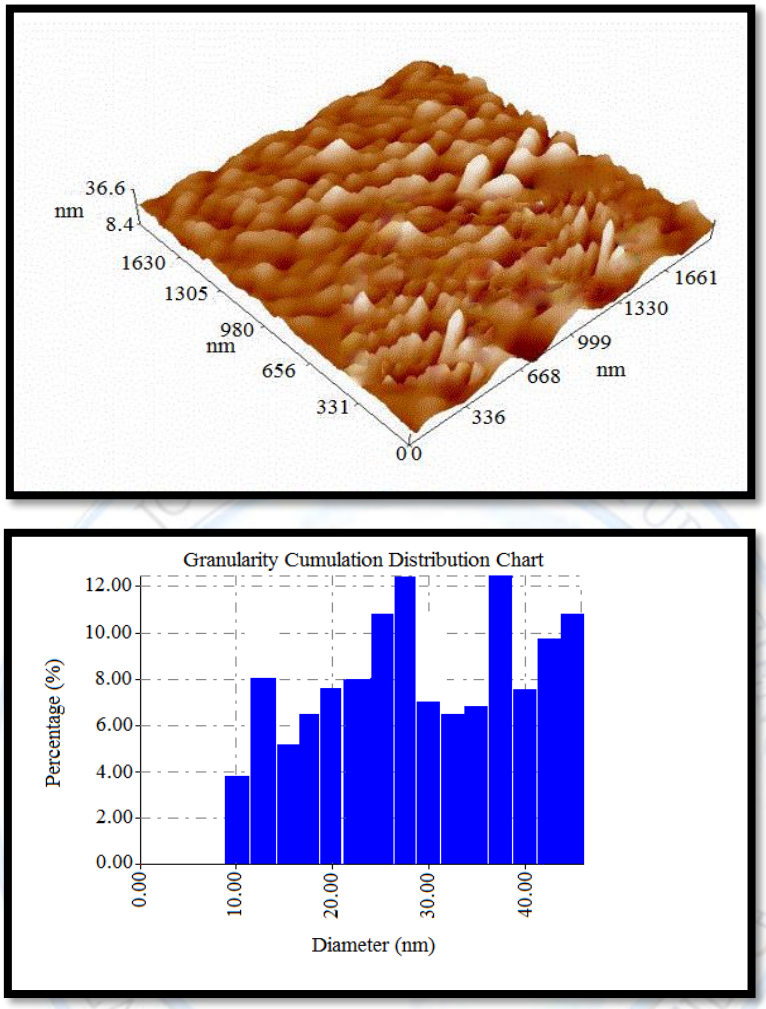


Figure 5: 3D image of AFM and granularity cumulative distribution chart for α-Fe_2O_3

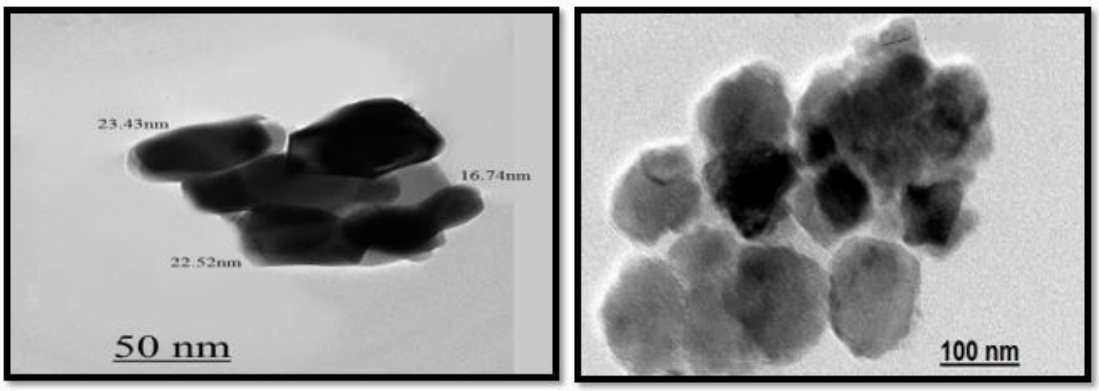


Figure 6: TEM of α-Fe_2O_3 nanoparticles

XRD analysis

Fig 7 shows the XRD patterns of it which that prepares by UV irradiation method. According to the standard XRD patterns (JCPDS 86-0550), the phase of ferric oxide was assigned to shape for crystal phase. All diffraction data of oxides from the resulting patterns indicate to hexagonal phase. The Debye-Scherrer formula [16] was used to calculate the crystal size of alpha phase and equal to 9.7nm by following equation:

$$D = k \lambda / \beta Cos\theta$$

Where k scherrer constant, λ is the wavelength of the Cu-Kα radiations, β is the full width at half maximum and θ is the angle obtained from 2θ values corresponding to maximum intensity peak in XRD pattern.

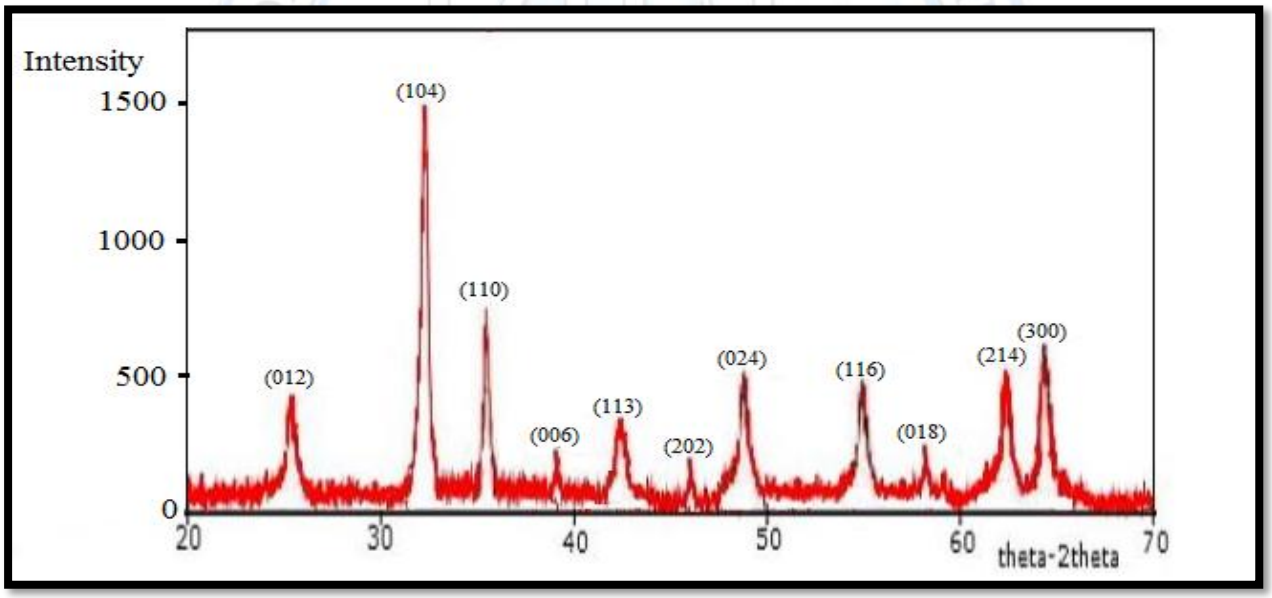


Figure 7: XRD of α-Fe_2O_3 NPs

Conclusion

In summary, α–Fe_2O_3 NPs was prepared by using UV irradiation process and it is an appropriate for creating it and its novel method for preparing. Many technique XRD, UV, AFM and TEM were used to character it, these techniques prove that the average of NPs of iron oxide size was from 10 to 45nm.

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