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The effect of doping Au on the magnetic properties of Fe_3O_4 NPs that prepared via photolysis and co-precipitation methods

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Abstract : Fe_3O_4 without Au was fabricated via photolysis method and then Au was doped with concentration 3 wt.% using co–precipitation method. The samples of Fe_3O_4 without/with Au doping were characterized by XRD, EDX, and TEM while the magnetic hysteresis loops of the samples were determined using PPMS. The results obtained a ferromagnetic demeanor at room temperature and fabrication of Fe_3O_4-Aunanoparticles as well as the resistance and the magnetic demeanor of the samples decrease with the doping of Au and that indicating semiconducting behavior. The saturation magnetization (MS) of the sample without doping (94.72 emu/g) is much higher than that (66.78 emu/g) of the sample with doping.
Key words : Doping, magnetite, nanoparticles, photolysis, co-precipitation.

Introduction

Through past few deeds, nanoparticles with magnetic properties have revolted noteworthy interest in many fields such as therapy [1,2], catalysis [3,4], protein purification and biological separation [5–7], target delivery [8,9], and biosensor [10,11]. The doped of Au on Fe_3O_4 surface, in particular, have enticed ever growing attention due to the noteworthy advantages for gold nanoparticles. For protecting magnetic nanoparticles, gold is an inert element and very useful for it. it has versatility in surface modification [12], unique biocompatibility [13], and high catalytic properties [14]. The physical and chemical properties of Au-Fe_3O_4 NPs is predominantly dependent on its particle size and morphology. Many pains have been made to synthesize Au-Fe3O4 NPs, such as preparation of oil phase [15–17], micro emulsion method [18,19], aqueous-phase method [20–22], and phase transfer [23,24]. Lately, the fabrication Au/Fe_3O_4 was announced by our group [25]. However, it is still of major benefit to design a low processing cost, simple manipulation and nontoxic method to get Au-Fe_3O_4 NPs with controllable size. Here, a two-step synthetic method was offered. First, nanoparticles of Fe_3O_4were fabricated by photolysis the ferric complex. Second, Au precursor were used to preparing doped material on the fe3o4 surface. The results obtained that the size of NPs ranged from 10 to 25 nm by controlling the power of irradiation.

2- Experimental part

2.1 Materials andinstruments

$[K_3(Fe(CN)_6].3H_2O$ (99%), $HAuCl_4.H_2O$ (99%) and NH_4OH (99%) were supplied from Sigma Aldrich and used without further purification. The morphology of NPs were determined using a transmission electron microscopy (JEOL JEM-2100 Japan). Element analysis, identity and size of particlesfor NPs were obtained using energy dispersive X-ray spectroscopy (EDX) analysis and X-ray diffract meter (XRD-6000) with copper Kαradiation respectively, while themagnetic properties of the showedNPs were characterized

by vibrating sample magnetometer (VSM, LakeShore 7073).

2.2 Synthesis of Fe_3O_4-AuNPs

The NPs of Fe3O4-Au were prepared through photolysis and co-precipitation methods. Briefly, 10gm of $[K_3(Fe(CN)_6].3H_2O$ was dissolved in 100ml distilled water. Then, 5ml of (0.1M) of NH4OH was added to the solution and it stirred until clear solution obtained. After that, the solution was irradiated for 2 hours using irradiation system that obtained at fig 1. Black precipitated was showed and left in solution. In the second beaker, 3% wt of $HAuCl_4$.H2O was dissolved in 100ml distilled water with adjusting the pH using ammonium solution and stirring the mixture for 30min. then, the precipitate solution of fabricated Fe3O4 was added to the solution of Au with stirring and adjusting the pH of the mixture by drops of NH_4OH. Finley, the precipitate solution was washed with water for several time until getting natural solution.

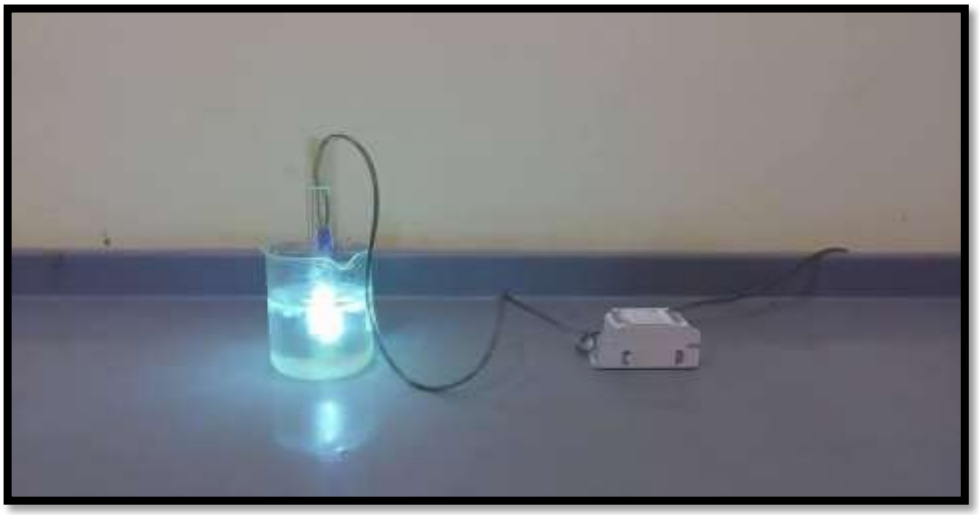

Fig. 1 The irradiation system

3- Result and Discussion

3.1 Fe_3O_4 with/without Au characterization

The structure of magnetite with/without gold were showed and studied using the spectra of XRD (fig. 2). All peaks that showed from (fig. 2a) was indicated to FCC shape and corresponded to Fe3O4 and it's in agreement with (JCPDS card No.79-0418) while the peaks at 38.42°, 44.91° and 64.62° angles that showed at (fig. 2b) assigned to the Au position and it's in agreement with (JCPDS card No: 04-0784). Due to the effect of doping and the weight of gold atoms, many peaks for magnetite such as 44.25° had been lost [26].Furthermore, the measurements of XRD show the high degree of crystallinity for NPs of Fe_3O_4/Au and that provided a reference of the morphology of the sample in detail and appear that Fe_3O_4NPs were single-phase.

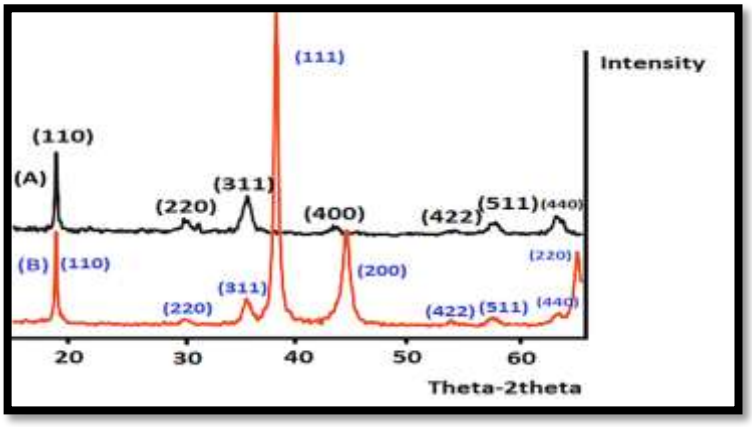

Fig. 2. XRD spectrum of pure magnitie (a), and magnetite with gold NPs (b)

The elements analysis of the samples were recorded using EDX spectrum and showed at (fig. 3a-b). The fig showed many peaks assigned to iron, oxygen, and gold and demonstrated to doping Au on the magnetite surface.

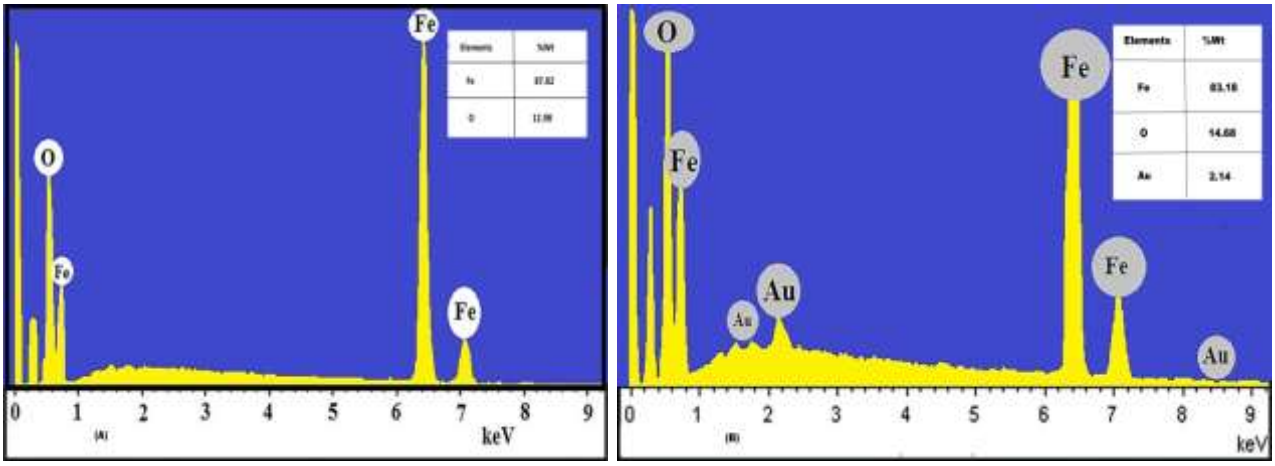

fig. 3. EDX spectrum of pure magnetite (a), and with gold (b)

shape and size of particles was showed at (fig. 4) and obtains TEM images listed from the fabricated Fe_3O_4–Au.The images obtained many atoms of gold that doped on the magnetite surface as displayed in below figures.

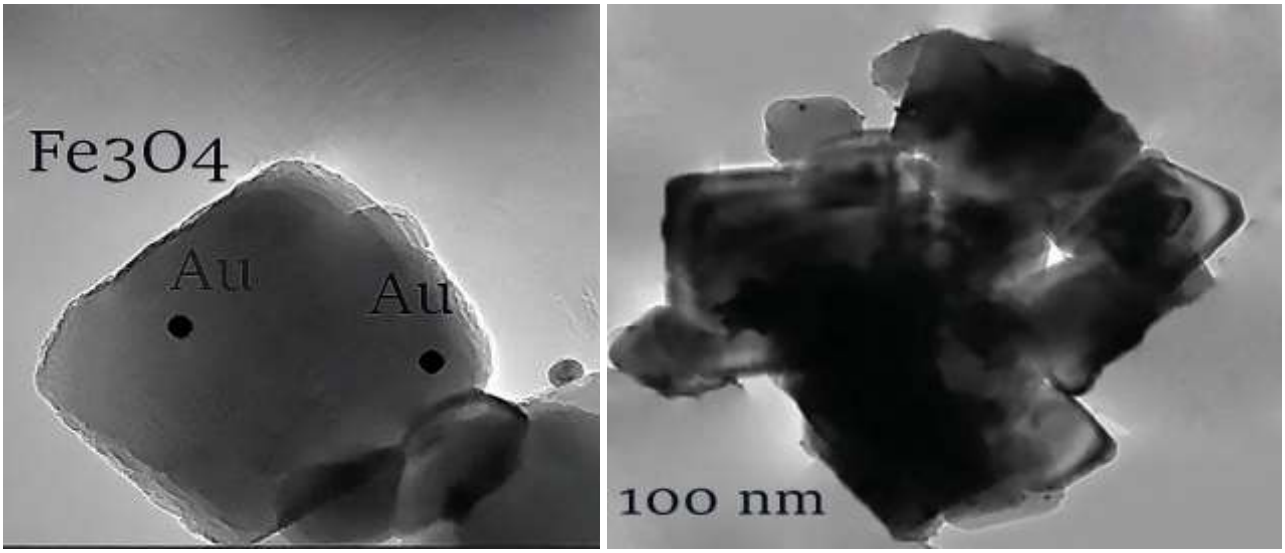

fig. 4. TEM of magnetite with gold (b)

3.2 The electric and magnetic study

After the characterization of the structure and phase of Fe_3O_4 with/without Au samples, the gauges of temperature-dependent resistance was recorded using standard four-probe. The comparison between resistances of samples appeared at (fig. 5) and showed decrease the resistance of Fe_3O_4 with Au sample and equal to (1.90 Ω)while (10.93 Ω) for pure magnetitedue to the mechanism of moving for electrons between Fe^{+2} and Fe^{+3} at B-sites and the moving of it depended on the activation energy and separation of ions.This phenomenon occurs when the surface of the material (Fe_3O_4) doped with another material (Au) and therefore reduced the resistivity.[27]

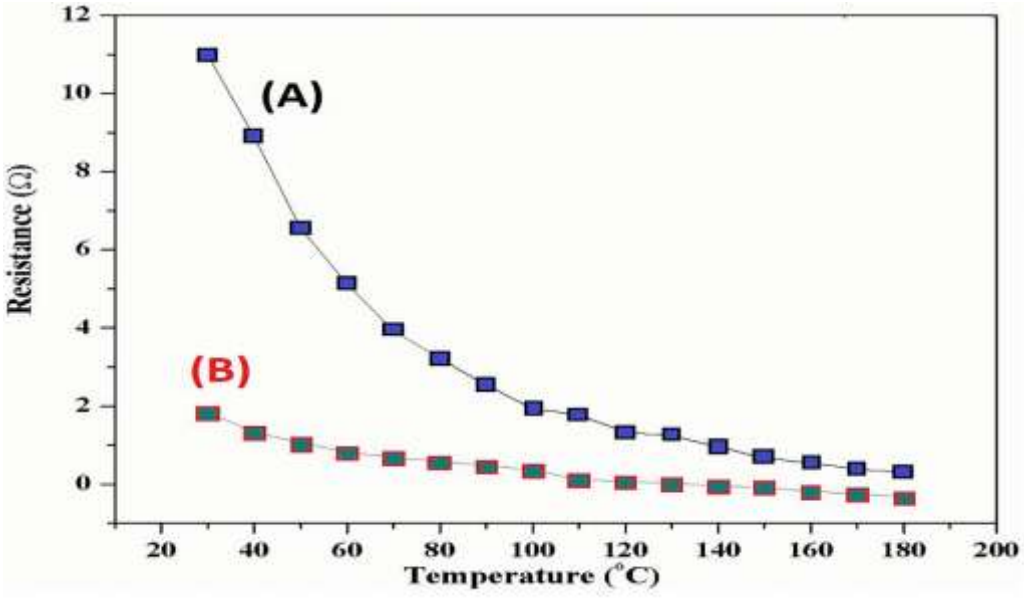

Fig. 5.Resistance versus temperature plot for pure Fe3O4 (a), and 3 wt.% Au/Fe3O4 (b)

The effect of doping Au upon the surface of magnetite was studied from results that showed at (fig. 6). From results, the samples show a clear ferromagnetichysteresisbehaviorwith/withoutAudoping and the saturation magnetization for pure magnetite (94.72 emu/g) is higher than doped with gold (66.78 emu/g) due to the non-magnetic behavior of Au. [27]

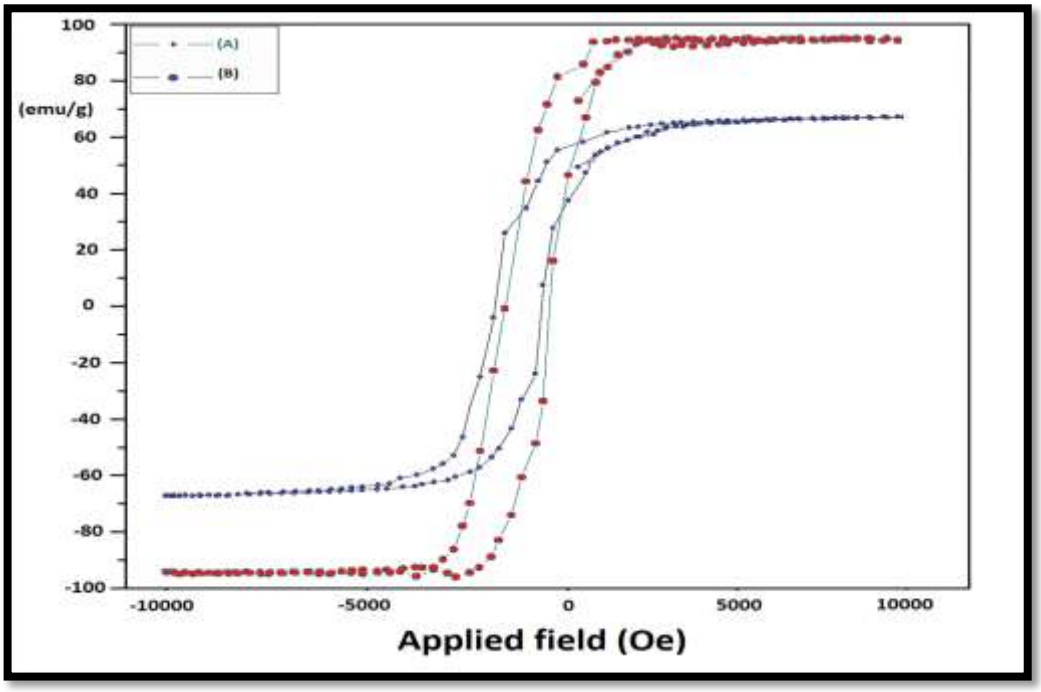

Fig. 6. M versus H plot for (a) pure Fe_3O_4, and (b) 3 wt.% Au/Fe_3O_4

Conclusion

In conclusion, we have proved a novel way for the preparation of Fe_3O_4-Au NPs with small size and high quality of particles. The surface morphology of samples was investigated by TEM and notice many atoms of gold doped upon the surface of magnetite while the amount of element before and after doped gold upon surface and the crystal lattice of samples was investigated by EDX and XRD respectively as well as the results obtained that the magnetic and resistance behaviors of magnetite decrease after doped gold and this indicating to semiconducting behavior.

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