Effect of Au doping on the Magnetic Properties of Fe_3O_4 NPs Prepared via Photolysis and co-Precipitation Methods

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Received: 24 October 2017 **Accepted: 15 January 2018**

Abstract

In this research, Fe_3O_4 without Au was fabricated via photolysis method, then Au was doped together with concentration of 3 wt.% using co–precipitation method. The samples of Fe_3O_4 without/with Au doping were characterized utilize XRD, EDX, and TEM while the magnetic properties of the samples were determined utilizing VSM. The results showed that the resistance and the magnetic values of the samples decrease with Au doping indicating semiconducting behavior. The saturation magnetization (MS) of the sample without doping (90.23 emu/g) is much greater than that (63.55 emu/g) of the sample with doping.

Keywords: Doping, magnetite, nanoparticles, photolysis, co-precipitation

DIYALA JOURNAL FOR PURE SCIENCES

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تأثير تطعيم الذهب على الخواص المغناطيسية للمغناتايت النانوي المحضر بطريقة التشعيع الضوئي والترسيب الكيميائي

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الخلاصة

في هذا البحث تم تحضير الماجنتايت بطريقة التشعيع الضوئي ومن ثم طعم بمادة الذهب بكمية 3% باستخدام طريقة الترسيب. الماجنتايت المطعم وغير مطعم بمادة الذهب تم تشخيصه باستخدام حيود الاشعة السينية، مطيافية تشتت الطاقة بالأشعة السينية و المجهر الالكتروني النافذ بينما شخص منحني التباطؤ المغناطيسي باستخدام نظام قياس الخواص المغناطيسية. بينت النتائج بوجود الخاصية المغناطيسية بدرجة حرارة الغرفة وتحضير الماجنتايت المطعم بعنصر الذهب، فضلا عن ان المقاومة والتوصيلية المغناطيسية للماجنتايت تقل عند تطعيمه بالذهب وهذا يدل على سلوك شبه موصل. واظهرت ايضا ان التشبع المغناطيسي بدون تطعيم (90.23 emu/g) اكبر من النموذج الذي تم تطعيمه (63.55 emu/g) .

الكلمات المفتاحية: التطعيم، الماجنتايت، الدقائق النانوية، التشعيع الضوئي، الترسيب المشارك

Introduction

Through past few decades, nanoparticles with magnetic properties have revolutionary 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 Au doping on Fe_3O_4 surface, has enticed growing regard due to the advantages of gold NPs. For protecting magnetic NPs, Au is an inert element and very profitable 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 predominantly rely on their particle size and morphology. Many methods have been made to synthesize Au-Fe_3O_4 NPs, such as preparation of oil phase [15–17], micro emulsion method [18, 19], aqueous-phase method [20–22]. Lately, fabrication of Au/Fe_3O_4 was announced by our group [23]. 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 fabrication method was offered. Firstly, the NPs of Fe_3O_4 were fabricated by photolysis of the ferric complex. Secondly, Au precursor was used to prepare doped material on the Fe_3O_4 surface.

Materials and Methods

Materials and instruments

$[K_3(Fe(CN)_6].3H_2O$ (99%), $HAuCl_4.H_2O$ (99%) and NH_4OH (99%) were supplied from Sigma Aldrich and used without further purification. The morphology of NPs was determined using a transmission electron microscopy (JEOL JEM-2100 Japan). Element analysis, identity and size of NPs were obtained using (EDX) spectroscopy and (XRD-6000) with copper Kα radiation respectively, while the magnetic properties of the NPs were characterized via vibrating sample magnetometer (VSM, LakeShore 7073).

Fabrication of Fe_3O_4-Au NPs

The NPs of Fe_3O_4-Au were prepared through photolysis and co-precipitation methods. Briefly, 10g of $[K_3(Fe(CN)_6].3H_2O$ was dissolved in 100ml of distilled water. Then, 5ml (0.1M) of NH_4OH was added to the solution and it is stirred until a clear solution is obtained. After that, the solution was irradiated for 2 hours using irradiation system (figure 1). Black precipitated of Fe_3O_4 was formed. In the second beaker, 3% wt. of $HAuCl_4.H_2O$ was dissolved in 100ml of distilled water with adjusting the pH using ammonium solution and stirring the mixture for 30min. Then, the precipitate solution of fabricated Fe_3O_4 was added to the solution of Au with stirring and adjusting the pH of the mixture (pH=9) by adding few drops of NH_4OH. Finally, the precipitate solution was washed with water for several times.

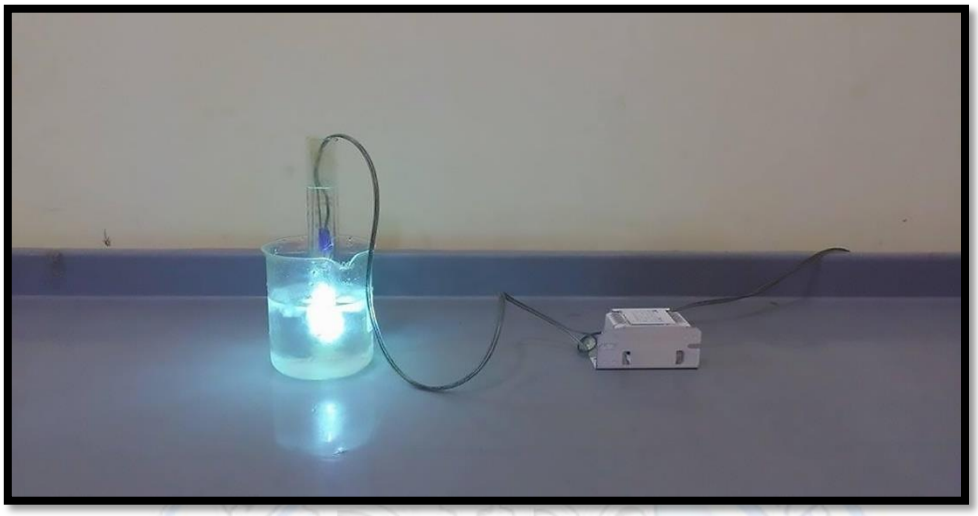

Figure 1: Irradiation system

Result and Discussion

Fe_3O_4 with/without Au characterization

The structure of magnetite with/without gold was studied using the patterns of XRD (figure 2). All peaks at (figure. 2A) are corresponded to Fe_3O_4 and face-centered cubic (fcc) structure and this is in agreement with (JCPDS card No.79-0418) while the sharp peaks were obtained at corresponding to the planes (111) and (220) indicates the doping Au ions (figure. 2B) and this is in agreement with (JCPDS card No: 04-0784). Due to the effect of doping and the weight of gold atoms, many peaks for magnetite had been lost with increasing doping [24]. Furthermore, the measurements of XRD show crystallinity with a high degree of Fe_3O_4/Au NPs.

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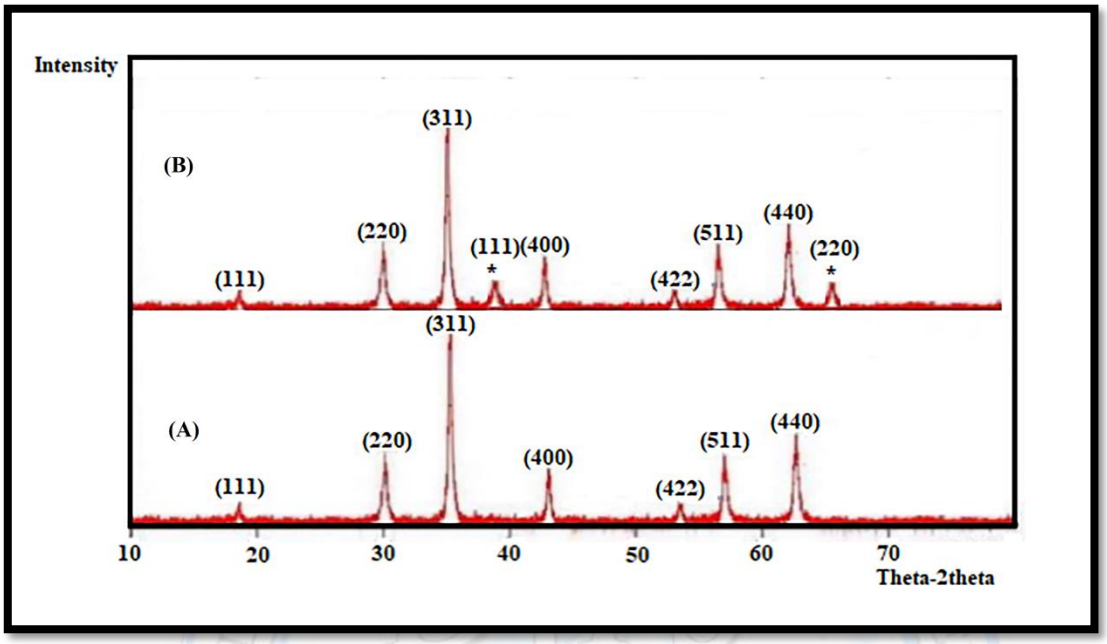

Figure 2: XRD patterns of (A) pure magnetite (B) and magnetite with gold NPs

The size of particles was determined utilizing the Scherrer's equation and it's listed in table1

$D = k \lambda / \beta Cos\theta$…….. (1)

Where k is Scherrer's 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.

Table 1: Size of particles for magnetite with and without Au

No.	Sample	Particle size
1	Fe_3O_4 without Au	21.57nm
2	Fe_3O_4 with Au	24.13nm

The elemental analysis of the samples was recorded using EDX spectrum as shown in (figure 3a-b). The figure showed many peaks assigned to iron, oxygen, and gold and proved doping the gold ions on the magnetite surface.

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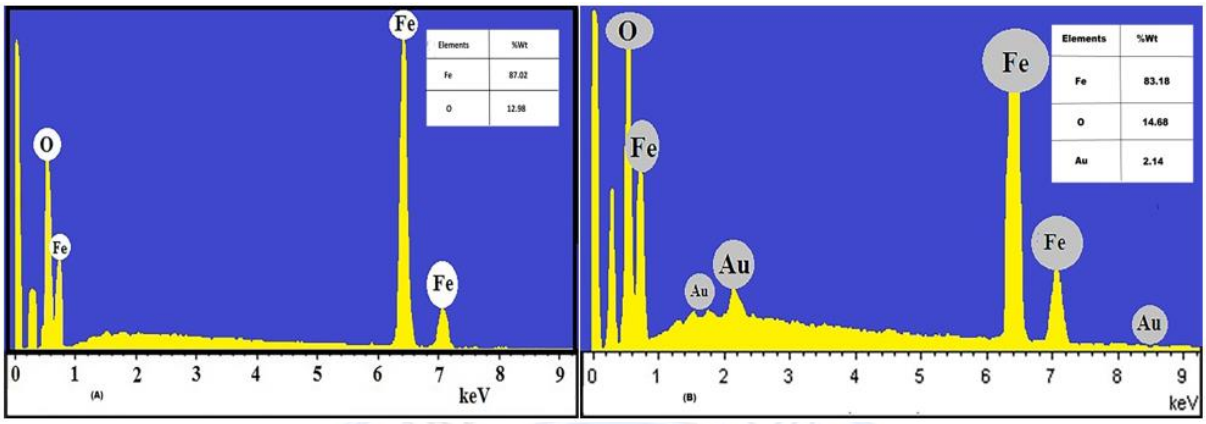

Figure 3: EDX spectrum of (a) pure magnetite and (b) magnetite with gold NPs

As shown in (figure 4)

Figure 4 shows TEM images of Au–doped Fe_3O_4 taken from the solution. The particles of Au are distributed on the surface of magnetite as shown in the same figures.

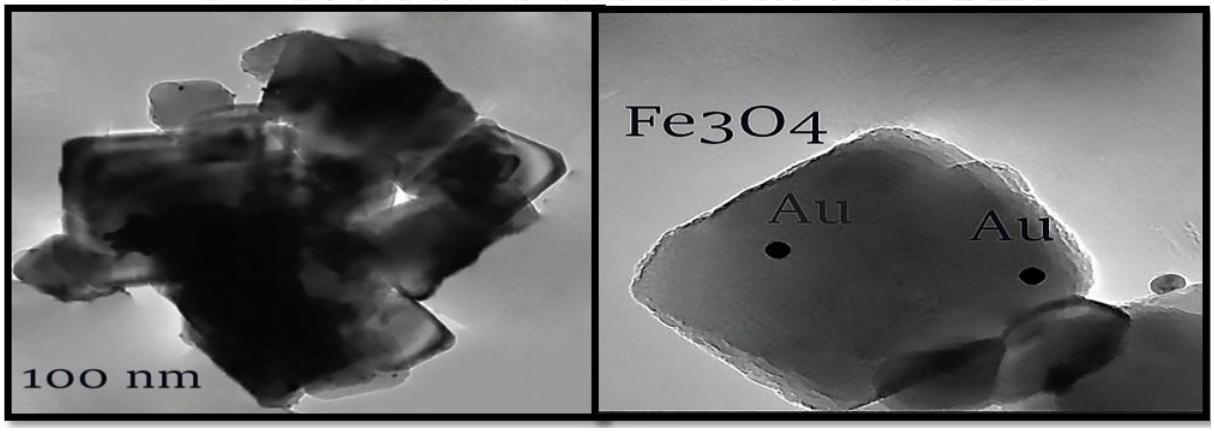

Figure 4: TEM of magnetite with gold

Study of the electrical and magnetic properties

The measurement of resistance-dependent temperature was recorded using standard four-point probe

$$\rho = Ae^{\frac{Eg}{2KT}} \ldots\ldots\ldots\ldots (2)$$

Where Eg: band gap of the material, T: Temperature in Kelvin, K Boltzmann constant, K – $8.6x10^{-5}$eV/K.

The comparison between the resistance of samples appeared at (figure. 5). From the results, the resistance of Fe_3O_4 was decreased with doping gold ions due to the mechanism of moving of electrons at B-sites between Fe^{+2} and Fe^{+3} depends on the activation energy and separation of ions. This phenomenon occurs when the surface of the material (Fe_3O_4) is doped with other material (Au) and therefore reduces the resistivity [25].

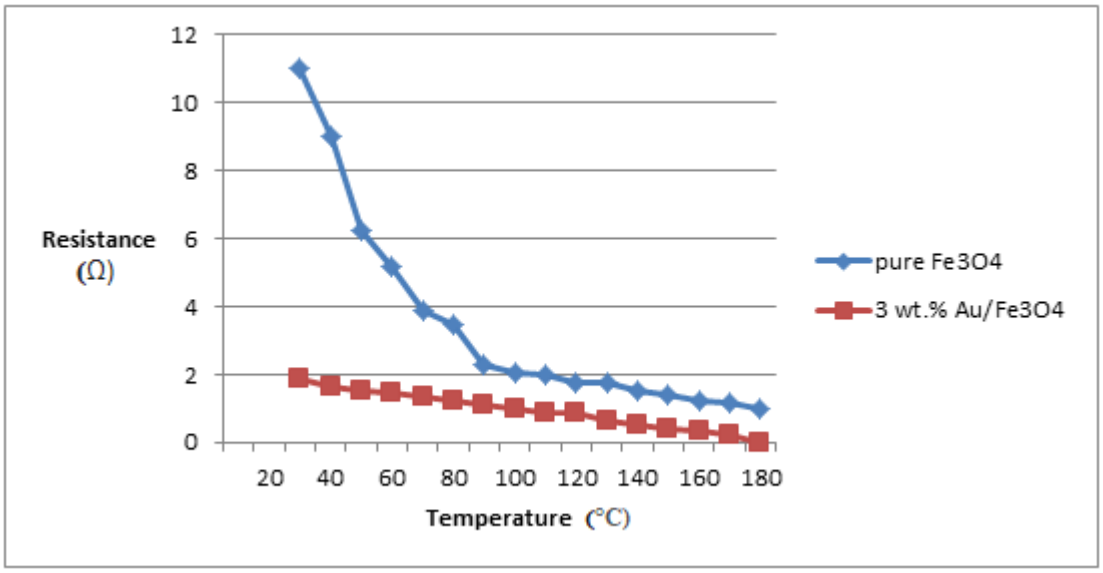

Figure 5: Relationship of resistance against temperature of pure Fe_3O_4 and 3 wt.% Au/Fe_3O_4

The effect of Au doping upon the surface of magnetite was studied from the results at (figure. 6). As can be seen, the magnetic behavior of Fe_3O_4 with/without Au doping are observed. The saturation magnetization of pure magnetite (90.23 emu/g) is higher than Au/Fe_3O_4 (63.55 emu/g) due to the non-magnetic behavior of Au.

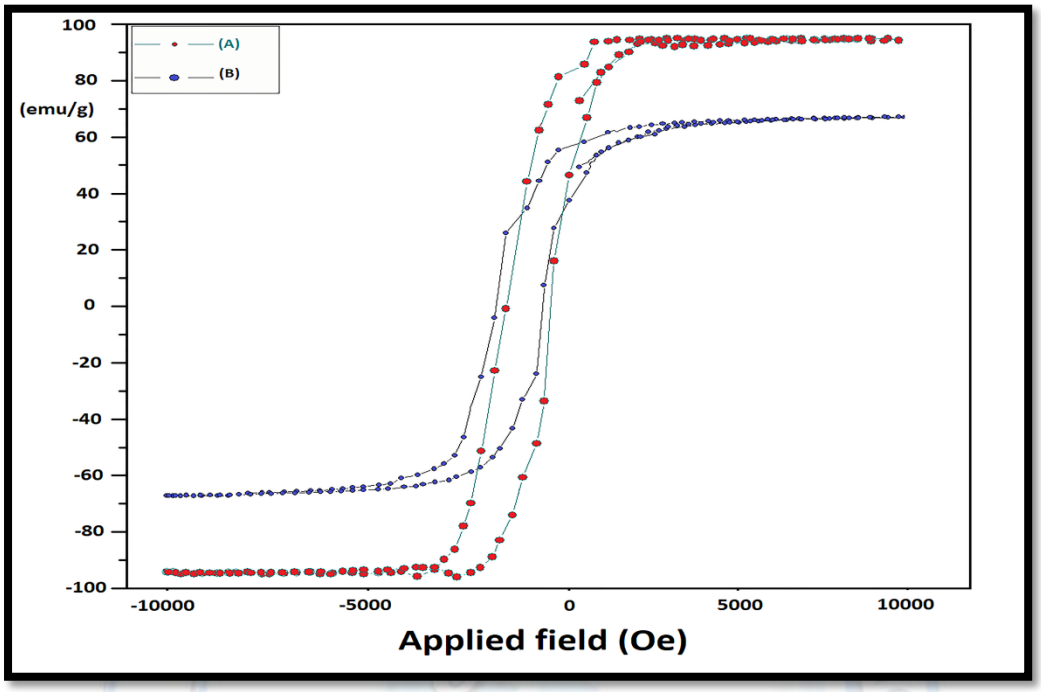

Figure 6: M against applied field plot of (a) pure Fe_3O_4, and (b) 3 wt.% Au/Fe_3O

Conclusion

In this study, we have provided a new way of preparation of Fe_3O_4-Au NPs with small size and high quality. The surface morphology of samples was investigated by TEM and no change in sample surface morphology was observed after Au doping while the amount of the element and the crystal lattice of samples were investigated by EDX and XRD respectively. However, the results showed that the resistance and magnetic values of Fe_3O_4 decrease sharply with the Au doping indicating semiconducting behavior.

Acknowledgement

The author thanks the chemist Farah Kefah Ali for encouraging him.

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