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Research paper

Preparation of Aniline Dimer-COOH Modified Magnetite (Fe_3O_4) Nanoparticles by Ultrasonic Dispersion Method

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Abstract

The magnetite (Fe_3O_4) nanoparticles capped with certain level of aniline dimer-COOH were prepared via assisted ultrasonic dispersion method and characterized by X-ray Diffraction spectra (XRD), Field Emission Scanning Electron Microscope (FESEM), Ultraviolent UV-visible (UV-vis) and Fourier Transformation Infrared spectroscopy (FTIR). The XRD result shows that both the sample of Fe_3O_4 nanoparticles synthesized without aniline dimer-COOH have similar peaks with the one that were capped with aniline dimer-COOH, this indicated the higher purity crystalline peaks of Fe_3O_4 nanoparticles was successfully synthesized. The Field Emission Scanning Electron Microscope (FESEM) result shows that, the aniline dimer-COOH modified magnetite nanoparticles are less agglomerated with spherical shape and continues size distribution, and the obtained image from EDS indicates the present of Fe_3O_4 nanoparticles by showing Fe-O group of element. The magnetic properties of the magnetite nanoparticles prepared by ultrasonic irradiation method was observed by vibrating sample magnetometer (VSM), the hysteresis loop of Fe_3O_4 nanoparticles observed by VSM has a saturation magnetization at 89.46 $emug^{-1}$ indicating super paramagnetic behavior of the Fe_3O_4 nanoparticles.

Keywords: *Magnetite Nanoparticles; Magnetic Properties; Morphologies; Ultrasonic Dispersion Method.*

1. Introduction

In the area of physics, chemistry, and materials science iron oxide nanoparticles play important roles [1]. Nanoparticles with sufficient magnetic properties served for many applications such as catalyst, magnetic recording media, and resonance imaging for clinical diagnosis [2]. However, the magnetite (Fe_3O_4) nanoparticle is one of magnetic nanoparticles prepared in various methods [3]. The ferrous ferrite or magnetite (Fe_3O_4, Fe_2O_3 or FeO) is an iron oxide that can be synthesized with different shape and size.

For most of application of the magnetite (Fe_3O_4) nanoparticles, uniform shape and size Fe_3O_4 nanoparticles are required to be well dispersed in the solvent. The major factors that influence the interest of many researchers, is the particles size which usually obtained by well-dispersed ultrasonic method. However, the shape and size of the Fe_3O_4 nanoparticles is usually controlled by their synthesis techniques. Therefore, these techniques is the most significant method for preparation certain materials, such as metal oxide powder and ceramic materials [4]. Furthermore, these technaques can used to produce suitable shape and size nanoparticles by capping with certain percentage of aniline dimer-COOH [5]. In a strategy to prepare Fe_3O_4 nanoparticles several synthesis methods are employed there include energy milling [6], sol-gel techniques [2], Co-precipitation method [7], Hydrothermal Techniques [8], and ultrasonic irradiation method [9], is the synthesis method for preparing most effective Fe_3O_4 nanoparticles with sufficient shape and size that can be used for many application [10]. As compared to the remaining conventional synthesis method ultrasonic techniques offer several advantages, such as overcoming of growth, nucleation and secondary process including attritions, breakage and agglomeration [11]. The Fe_3O_4 nanoparticles produce by the remaining synthesis techniques are relatively broad with continues size distribution, although it is very difficult to prevent the nucleation during the upcoming growth of nuclei [12]. On the other hand, ultrasonic irradiation techniques can help to decrease the particles sizes of Fe_3O_4 nanoparticles to the extent that can be used for many applications such as ferrofluid, magnetic recording media, and sensing application [13, 14]. many attempt has been made to prepare magnetite (Fe_3O_4) nanoparticles using cheapest material $FeCl_2$ and $FeCl_3$, but in many case has not been achieved [15], in our experiment Fe_3O_4 nanoparticles capped aniline dimer-COOH was successfully synthesized using the same materials and Fe_3O_4 nanoparticles were observed. In recent time, the magnetite nanoparticles are prepared to be used as a solution to certain environmental problems and many experimental researches was carryout demonstrating the preparation of Fe_3O_4 nanoparticles and used for wastewater treatment, such as adsorb cadmium, nickel, and crom [16, 17].

This research, aims to demonstrate the preparation of magnetite (F_3O_4) nanoparticles capped with certain quantity of aniline dimer-COOH by ultrasonic irradiation method. The capping effect was observed by Field Emission Scanning Electron Microscopy (FESEM), the morphology of Fe_3O_4 capped aniline dimer-COOH is less agglomerated and more spherical. Furthermore, these nanoparticles was also characterized by Fourier Transformation Infrared spectra (FTIR), X-ray diffraction (XRD), ultraviolet-visible (UV-vis) and the magnetic properties of Fe_3O_4 nanoparticles were

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examined by Vibrating Sample magnetometer (VSM), the result shown super paramagnetic nature of the magnetite nanoparticles. Table1, tabulate the synthesis of Fe_3O_4 nanoparticles with certain level aniline dimer-COOH, prepared by ultrasonic dispersion method.

2. Materials and Methodology

All reagents were analytical grade, and used without further purification, including ferric chloride ($FeCl_3$), ferrous chloride ($FeCl_2$) ammonium hydroxide (NH_4OH) N-phynyl-1,4-phenylenediamine, Succinic anhydride, Diethyl ether, dichloromethane CH_2Cl_2 and methanol.

2.1. Synthesis of Aniline dimer-COOH

The aniline dimer-COOH was prepared in the 3-necked round bottom flask 100 ml equipped with mechanical stirrer nitrogen inlet and outlet. Succinic anhydride 4.3 g and 0.823 g of N-phenyl-1,4-phenylenediamine were dissolved in 30 ml of dichloromethane (CH_2Cl_2) under magnetic stirrer at room temperature for a period of 6h. As the reaction proceeded, a white grey precipitate was obtained. Finally, the precipitated was collected by filtration and washing with diethyl ether until the filtrated become colourless. The product was dried in vacuum at room temperature for 24h.

2.2. Synthesis of Fe_3O_4 nanoparticles

The magnetite (Fe3O4) nanoparticles were synthesized as followed , 4.7 g of iron (III) chloride ($FeCl_3 .6H_2O$) and 1.72 g of iron (II) chloride ($FeCl_2 .4H_2O$) were dissolved under N_2 in distilled deionized water 60 ml under ultrasonic disperser for a period of 1h. As the solution is heated to 30 ^{0}C, 10 ml of NH_3 was added, subsequently followed by addition of solution of aniline dimer-COOH 400 mg in 4 ml of acetone. The reaction was allowed to proceed for 1.5h at 50 ^{0}C with vigorous starring to obtained stable water base suspension. The reaction was allowed to cool to room temperature. The suspension was later washed subsequently with water, ethanol and acetone.

Table 1: Magnetite (Fe_3O_4) capped with different level of aniline dimer-COOH

Samples	Fe^{3+} + Fe^{2+} (g)	NH3 (ml)	Aniline dimer-COOH (g)
S1	2.0	05	0.0
S2	2.5	10	0.4

3. Characterization

The crystalline phase of the magnetite (Fe_3O_4) nanoparticles was characterized by X-ray diffraction (XRD), Shimadzu XD-610. At a radiation wavelength of (λ = 0.14506 nm), the pattern were recorded at the range of 10 to 90^0, the Fe_3O_4 nanoparticles morphologies of the particles was examined by Field Emission Scanning Electron Microscope (FESEM) (FESEM JEOL model JDM 7600F) equipped with Energy dispersive spectrometer (EDS). The magnetic properties of the magnetite nanoparticles were measure at room temperature by Vibrating Sample Magnetometer (VSM) 74004 Lakeshore. However, the Fourier Transform Infrared Spectrum (FTIR) (Perkin Elmer Spectrum 100 FTIR spectrometer) are use to observe the molecular structure of the Fe_3O_4 nanoparticles. The absorption band of the magnetite nanoparticles samples were measured by (HITACHI3900H) Ultraviolet (UV-vis).

4. Results and Discussion

4.1 The analysis pattern of XRD in magnetite (Fe_3O_4) nanoparticles

The crystalline phase of Fe_3O_4 nanoparticles were examined by X-ray diffraction (XRD) as shown (Fig. 1) at a diffraction peak of 2 = 35.611^0, 32.67^0, 63.05^0, 70.49^0, and 77.22^0. This can be assigned to (311), (400), (422), and (440), planes of Fe_3O_4 in the Bragg reflection respectively, and were also compared with standard magnetite XRD pattern (JCPDS98-026-3011). This reveals the resultants nanoparticles is purely Fe_3O_4 nanoparticles [18], the most intense peaks (311) of magnetite phase appear in all the samples can be used for crystal evaluation. S1 is the plot of ordinary Fe_3O_4 nanoparticles whiles S2, are the plot of aniline dimer-COOH capped Fe_3O_4 nanoparticles prepared by ultrasonic dispersion method [19], No impurity peak was observed, indicating that high purity crystalline Fe3O4 was successfully synthesized.

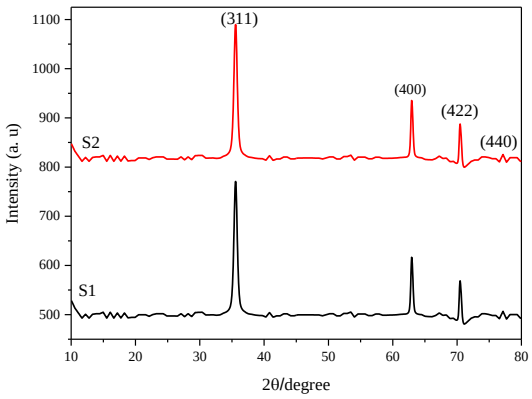


Fig. 1: XRD analysis of Fe_3O_4 nanoparticles shows the variation of aniline dimer-COOH

4.2 Fourier Transformation Infrared Spectra (FTIR) analysis

The IR spectra The IR spectra of the Fe_3O_4 nanoparticles prepared with assisted aniline dimer-COOH is shown in figure 2(S1) while S2 is the corresponding plot of magnetite nanoparticles prepared without aniline dimer-COOH, resulted in the formation of Fe-O bands which is proven by the appearance of the absorptions band at 523 cm^{-1} in S1 and, 530 cm^{-1} in sample (S1, and S2) respectively[20]. In the aniline dimer-COOH capped Fe_3O_4 nanoparticles some functional group of C=O is observed which is due to stretching vibration of the carboxylic group, revealing between 1469 cm^{-1}to 1634cm^{-1} for S1 and S2 indicating that the aniline dimer-COOH is in salt form. A wider bonds appear at 3370 cm^{-1} in both S1 and S2 which is due to vibrating stretching may be attributed to the H_2O molecules or O-H [21].

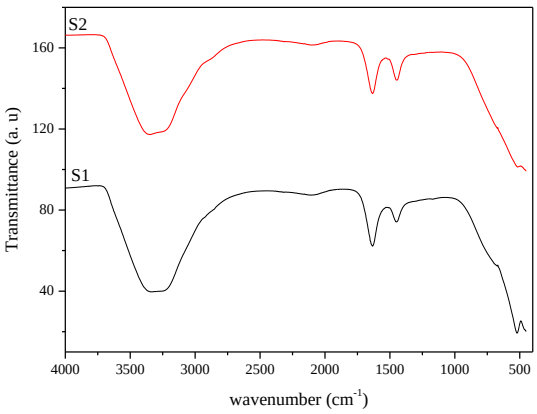


Fig. 2: FTIR analysis of Fe_3O_4 nanoparticles shows the variation of capped aniline dimer-COOH

4.3. Field Emission Scanning Electron Microscope (FESEM) image of magnetite (Fe_3O_4) nanoparticles and EDS image

The morphologies of the (Fe_3O_4) nanoparticles were observed by FESEM, the obtained image is shown in (Fig. 3. a, b, c).The Fe_3O_4 nanoparticles are appeared to be in a spherical structure when capped with aniline dimer-COOH. However, the spherical nanoparticles exhibit magnificent internationalization rate and highest cellular uptake instead of another shape such as nanorods, nanocubes or nanodisk [18]. Moreover, due to strong interparticles Van der Waals force and magnetic attraction among the Fe_3O_4 nanoparticles, some agglomeration is detected in the samples. However, the image of EDS is shown in Fig.3(d) indicates the present Fe_3O_4 by shown Fe-O group.

which is corresponding to π-π* transition in the benzenoid ring of the aniline dimer-COOH observed at [22]. Furthermore, the magnetite nanoparticles samples capped with certain level of aniline dimer-COOH were severally washed with acetone and ethanol which resulting in dissolving aniline dimer-COOH completely this

data indicated clearly that there is some interaction between Fe_3O_4 nanoparticles and aniline dimer-COOH[22].

4.4. Ultraviolent UV-vis analysis

The UV-vis spectra were used to analyse the structure of the resulting aniline dimer-COOH modified magnetite (Fe_3O_4) nanoparticles, as well as the Fe_3O_4 nanoparticles prepared with absent of aniline dimer-COOH, the absorption was found at a wavelength of 365 nm

4.5. Magnetic Properties

The magnetic properties of the magnetite nanoparticles prepared via ultrasonic irradiation method were measured using Vibrating Sample Magnetometer (VSM) at room temperature (25 ^{0}C). The resulting magnetization curve is shown in the Fig. 5.

The Fe_3O_4 nanoparticles demonstrate super paramagnetic performance with saturation magnetization of 89.46 emu g^{-1}. This saturation magnetization of Fe_3O_4 nanoparticles is almost similar to the actual saturation magnetization of Fe_3O_4 reported in the literature by [16]. The hysteresis loops indicated that the Fe_3O_4 nanoparticles are super paramagnetic in nature. Zero remanence, coercivity and reversible hysteresis behavior indicating super paramagnetic nature of the Fe_3O_4 nanoparticles.

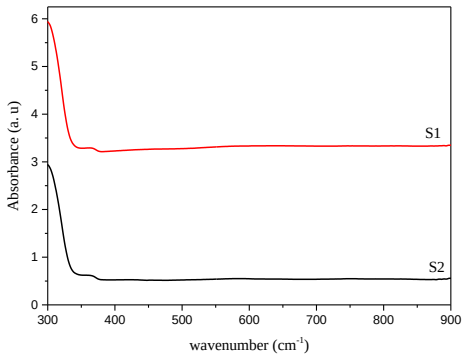


Fig. 4: UV-vis Analysis of Fe_3O_4 nanoparticles

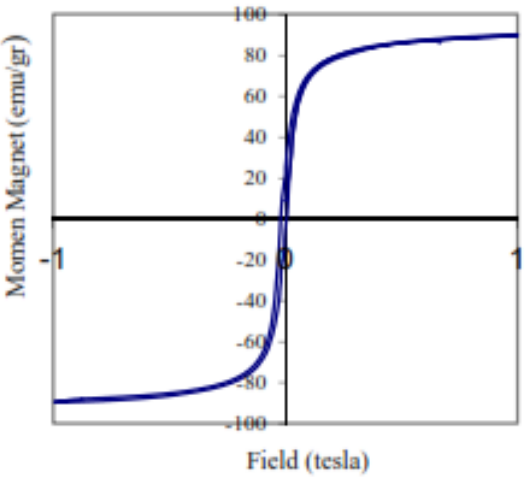
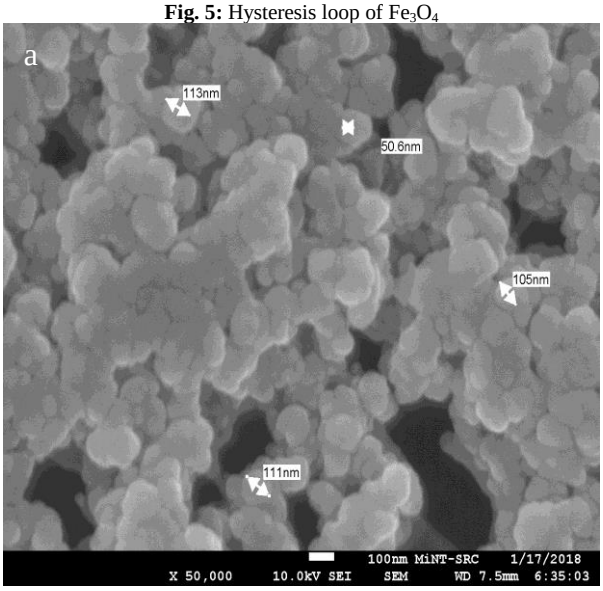
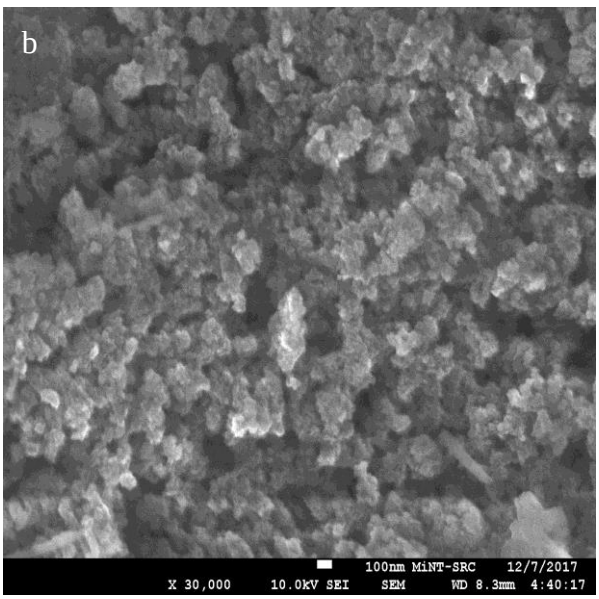


Fig. 5: Hysteresis loop of Fe_3O_4





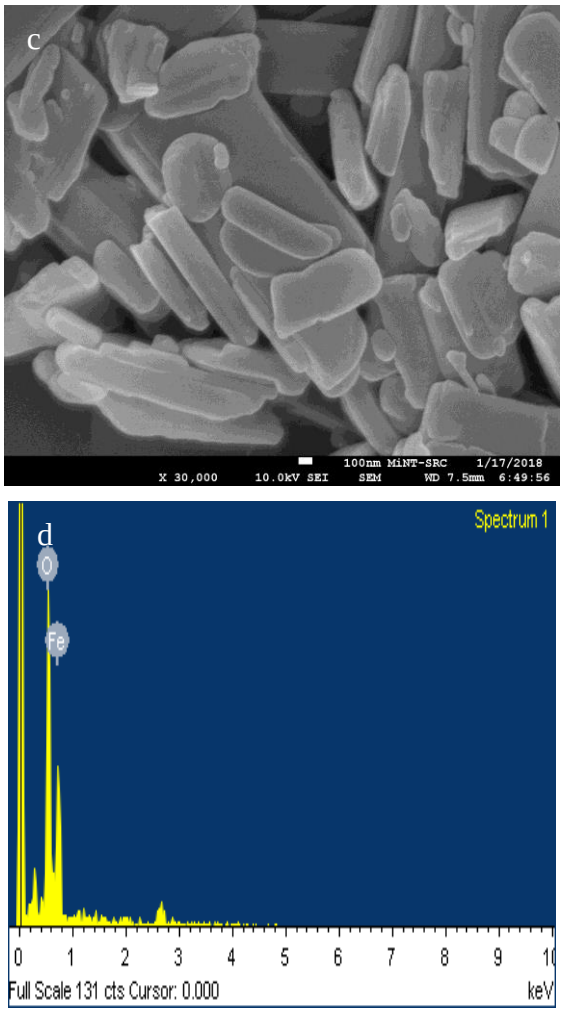


Fig.3: FESEM image of Fe_3O_4 nanoparticles capped aniline dimer-COOH (a) Fe_3O_4 nanoparticles uncapped aniline dimer-COOH (b) morphologies of aniline dimer-COOH (c) and image of EDS (d)

5. Conclusion

In this experiment we have demonstrated the preparation of aniline dimer-COOH modified magnetite (Fe_3O_4) nanoparticles through ultrasonic dispersion method. The modification of the prepared Fe_3O_4 nanoparticles with certain level of aniline dimer-COOH was observed by Field Emission Scanning Electron Microscope (FESEM) and subsequently characterized by XRD, FTIR, UV-vis and the magnetic properties of the magnetite nanoparticles was observed by vibrating sample magnetometer (VSM). It was observed that Fe_3O_4 nanoparticles modified with aniline dimer-COOH is quite more spherical and less agglomerated compared with pure Fe_3O_4 nanoparticles. The results found in the XRD analysis indicate that there is no impurity peaks observed in the prepared magnetite nanoparticles. The hysteresis loop of Fe_3O_4 nanoparticles observed by VSM shows saturation magnetization behaviour at 89.46 $emug^{-1}$.

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