

# Preparation of amine-modified Fe<sub>3</sub>O<sub>4</sub>/carbon nanoparticles by submerged arc discharge in ethylenediamine/ethanol

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**Abstract.** The preparation of amine-modified iron oxide/carbon (Fe<sub>3</sub>O<sub>4</sub>/C) nanoparticles was performed by the submerged arc discharge method using graphite electrodes and a liquid medium consisting of 50% ethanol and added ethylenediamine. The arc discharge was conducted by passing a voltage of 20–40 V. Two graphite electrodes were used, where one of them was filled with Fe<sub>3</sub>O<sub>4</sub>, carbon graphite and binder in a mass ratio of 1:3:1. The properties of the fabricated Fe<sub>3</sub>O<sub>4</sub>/C nanoparticles were analysed using X-Ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The XRD diffractogram pattern of the prepared Fe<sub>3</sub>O<sub>4</sub>/C showed definitive peaks at 26.5238° and 35.6374°, which are the main characteristic peaks of C graphite and Fe<sub>3</sub>O<sub>4</sub>, respectively. SEM analysis showed that the nanocomposite had a spherical morphology. TEM analysis found that the structure of the nanocomposite was Fe<sub>3</sub>O<sub>4</sub>-coated carbon.

## 1. Introduction

Magnetic nanoparticles (MNPs) are of great interest for researchers from a wide range of fields, including those working in magnetic fluids, catalysis, biotechnology/biomedicine, magnetic resonance imaging, data storage and environmental remediation [1]. Recently, iron oxide (Fe<sub>3</sub>O<sub>4</sub>) MNPs have been intensively investigated because of their superparamagnetism, high coercivity and low Curie temperature [2–5].

In addition to these characters, Fe<sub>3</sub>O<sub>4</sub> MNPs are non-toxic. These simple nanoparticles are vulnerable to rapid degradation in the environment due to the high surface area to volume and reactivity ratios. One way to protect nanoparticles from degradation is by coating them with a stable chemical species, such as graphite. Carbon is one of the best solutions for encapsulation because it is light, inexpensive and very stable under extreme chemical or physical environments. The carbon layer protects the nanoparticles from environmental degradation so as to retain their intrinsic nanocrystalline properties [6].

Magnetic carbon nanoparticles are synthesized using several methods, such as arc discharge [7], microwave heating [8], thermal plasma [9], explosion [10], chemical vapour condensation [11] and hydrothermal reaction [12]. In this paper, the arc discharge method was used to synthesize Fe<sub>3</sub>O<sub>4</sub>/C



because it is a simple, convenient and economical method [13]. According to Sano (2002), the arc-discharge method in liquid media, as opposed to a vacuum system, will produce nanomaterial products with a high level of purity [14].

Carbon-based MNPs are hydrophobic, whereas in biological applications they must be hydrophilic. Therefore, surface modification is needed to make the nanoparticles hydrophilic, which will allow them to be coated with useful molecules, such as antibodies [15]. Amino-group functionalization is suitable for graphite because of its ability to enhance the reactivity and hydrophilic nature of the nanoparticles [16]. These magnetic nanoparticles has superparamagnetic property, which means they will only be magnetic when present in a magnetic field. The amine-group functionalization allows the nanoparticles to have hydrophilic surfaces allowing for an easy dispersion, and preventing clumping without losing its magnetic property [17–18].

In this work, the surface of  $\text{Fe}_3\text{O}_4/\text{C}$  nanoparticles were synthesized and modified in one step via the arc discharge method in a liquid medium. The amine-modified  $\text{Fe}_3\text{O}_4/\text{C}$ , prepared by adding ethylenediamine into the ethanol medium, provided an attachment point for an amine functional group on the nanocomposite surface. Additionally, ethylenediamine is expected to improve the hydrophilic properties of the  $\text{Fe}_3\text{O}_4/\text{C}$  nanoparticles. This should make the nanoparticles more biocompatible, allowing them to be used for bio-applications, such as coating them with useful molecules like antibodies.

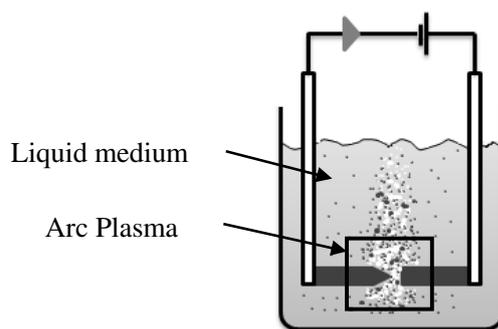
## 2. Experimental details

### 2.1. Materials

The materials that were used for fabrication process include carbon electrodes, carbon powder, iron oxide ( $\text{Fe}_3\text{O}_4$ ), 99% ethylenediamine (Merck), 70% ethanol (technical grade), fructose binder (technical grade), and deionized water.

### 2.2. Fabrication of $\text{Fe}_3\text{O}_4/\text{C}$ nanoparticles

A modified graphite electrode as the anode was filled with a mixture of  $\text{Fe}_3\text{O}_4$ , carbon powder and fructose binder in a ratio of 1:3:1 (w/w/w). This modified electrode was heated at  $180^\circ\text{C}$  for six hours. The cathode was made from a graphite electrode with a sharp tip.



**Figure 1.** Experimental setup for the fabrication of amine-modified  $\text{Fe}_3\text{O}_4/\text{C}$  nanoparticles via the arc discharge method.

The cathode and anode were placed a certain distance apart in 2 mm in order to achieve the arcing. A liquid medium consisting of 50% ethylenediamine and 50% ethanol in 300 mL total volume was used.

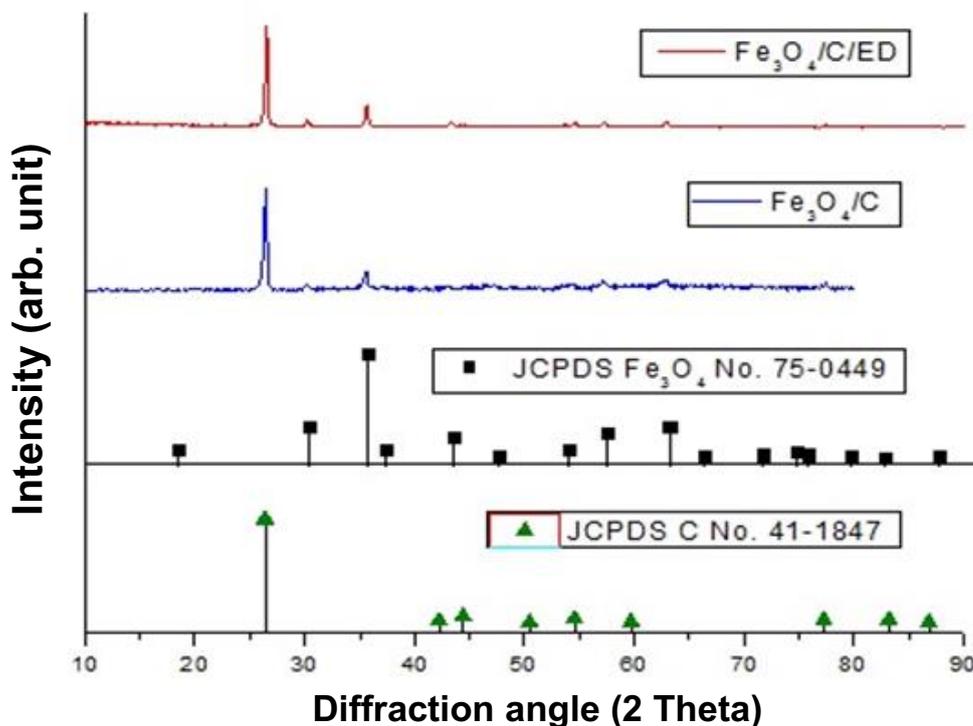
The fabrication process was carried out using 20 V with 10 A of current. The experimental set-up is presented in Figure 1.

The  $\text{Fe}_3\text{O}_4/\text{C}$  nanoparticles produced were collected and further characterized by X-ray diffraction (XRD) (Cu; 40 kV; 35 mA) to determine their crystallinity and crystal structure. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to identify the surface structure morphology, particle size and to determine the structure of the nanoparticles. Dispersion tests were also performed to determine the quality of the nanoparticle dispersion prepared from the fabrication process.

### 3. Results and discussion

Preparation and amino-group surface modification of the  $\text{Fe}_3\text{O}_4/\text{C}$  nanoparticles were successfully achieved using the arc discharge method in a liquid medium. When an electrical current was passed from the cathode to anode, the electrical ions produced an arc that leaped between both electrodes. During this process, the  $\text{Fe}_3\text{O}_4$  and carbon present in the prepared electrodes were evaporated in the hot arc zone and then condensed to a nanocomposite in the cooler surrounding zone. This interaction produced amine-modified  $\text{Fe}_3\text{O}_4/\text{C}$  nanoparticles.

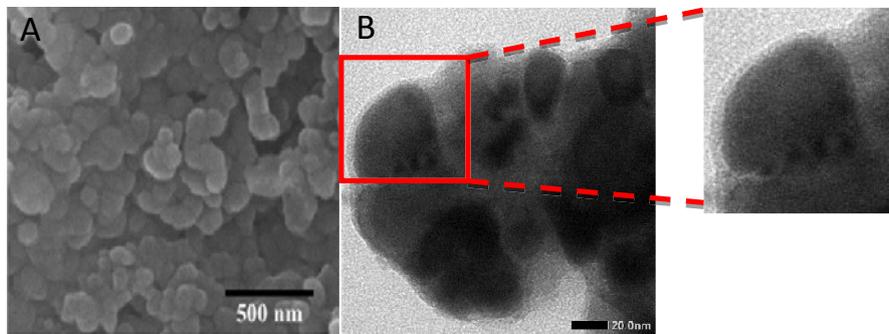
Following the fabrication process, the  $\text{Fe}_3\text{O}_4/\text{C}$  nanoparticles were characterized using XRD to determine the crystallinity changes after fabrication and surface modification. The XRD patterns for the  $\text{Fe}_3\text{O}_4/\text{C}$  and amine-modified  $\text{Fe}_3\text{O}_4/\text{C}$  nanoparticles are shown in Figure 2.



**Figure 2.** X-ray diffraction (XRD) patterns of  $\text{Fe}_3\text{O}_4/\text{C}$  and amine-modified  $\text{Fe}_3\text{O}_4/\text{C}$  ( $\text{Fe}_3\text{O}_4/\text{C-ED}$ ).

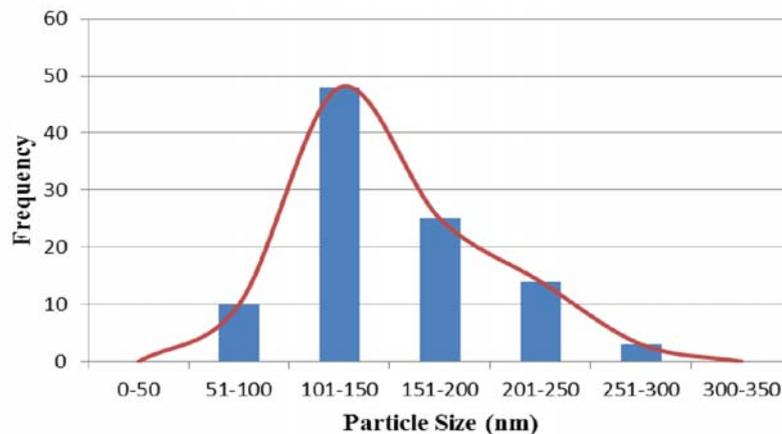
The diffractogram of the amine-modified  $\text{Fe}_3\text{O}_4/\text{C}$  shows peaks comparable to those in the Joint Committee on Powder Diffraction Standards (JCPDS) pattern. The peak at  $2\theta$  of 26.38 (002) is the main peak characteristic of carbon (JCPDS No. 41-1487), and the one at 35.76 (311) is the main peak characteristic of  $\text{Fe}_3\text{O}_4$  (JCPDS No. 75-0449). The main peaks for both  $\text{Fe}_3\text{O}_4$  and carbon existed in the XRD pattern of the amine-modified  $\text{Fe}_3\text{O}_4/\text{C}$ , as well as in the  $\text{Fe}_3\text{O}_4/\text{C}$ , indicating that the both of nanoparticles were composed of crystalline  $\text{Fe}_3\text{O}_4$  and elemental carbon.

The images of the amine-modified  $\text{Fe}_3\text{O}_4/\text{C}$  nanoparticle were analysed using SEM and TEM, and the results are shown in Figure 3. Figure 3A shows the SEM image of an amine-modified  $\text{Fe}_3\text{O}_4/\text{C}$  demonstrating a spherical morphology. The structure of these nanoparticles was further observed in detail by TEM, as shown in Figure 3B. The  $\text{Fe}_3\text{O}_4/\text{C}$  nanoparticles were observed to be nanoparticles coated by carbon layers. The imaging results shown in Figure 3 have a good agreement with the XRD pattern, which shows that the produced nanoparticles consisted of  $\text{Fe}_3\text{O}_4$  and carbon.



**Figure 3.** (A) SEM and (B) TEM images of amine-modified  $\text{Fe}_3\text{O}_4/\text{C}$ .

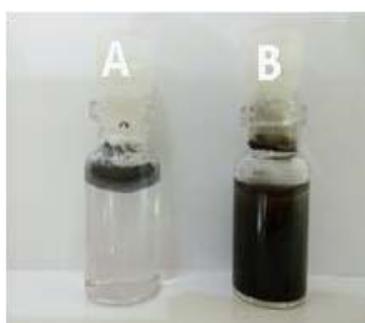
Figure 4 shows the histogram of the particle cluster size of the amine-modified  $\text{Fe}_3\text{O}_4/\text{C}$ , as measured from the SEM images in a spot observation (the images are not shown here). The diameter of the particle cluster size of the amine-modified  $\text{Fe}_3\text{O}_4/\text{C}$  produced using arc discharge has a dominant size range of 100–150 nm as an agglomerated formation, indicating that the particles produced are nanoparticles because each particle diameter is probably less than 100 nm in size.



**Figure 4.** Histogram of particle cluster size of amine-modified  $\text{Fe}_3\text{O}_4/\text{C}$ .

In order to visually observe the successful surface modification, the produced nanoparticle was dispersed in distilled water. The purpose of this dispersity test, shown in Figure 5, was to determine the quality of the dispersion of the material produced using this fabrication process. Figure 5 compared the dispersion of  $\text{Fe}_3\text{O}_4/\text{C}$  produced using submerged arc discharge in ethanol and  $\text{Fe}_3\text{O}_4/\text{C}$  produced using submerged arc discharge in ethanol with addition of ethylenediamine.

The dispersion test pictured in Figure 5A and 5B showed that the  $\text{Fe}_3\text{O}_4/\text{C}$  produced in ethanol/ethylenediamine has a better dispersity in the aqueous liquid medium than the  $\text{Fe}_3\text{O}_4/\text{C}$  produced in ethanol only. These latter particles remained on the top of the water surface, while the amine-modified particles were dispersed completely, as indicated by the darker liquid.



**Figure 5.** Dispersion test of (A) unmodified  $\text{Fe}_3\text{O}_4/\text{C}$  produced using submerged arc discharge in ethanol only (B) and amine-modified  $\text{Fe}_3\text{O}_4/\text{C}$  produced using submerged arc discharge in ethanol/ethylenediamine.

This clearly demonstrates that the nanoparticles that had a better dispersion have a hydrophilic surface character provided by amino groups attached to the nanoparticles' surfaces, called the amine-modified  $\text{Fe}_3\text{O}_4/\text{C}$ . The amino groups contained in the ethylenediamine/ethanol liquid medium were successfully attached to the nanoparticle surface during the arc discharge process. On the other hand, the unmodified  $\text{Fe}_3\text{O}_4/\text{C}$  nanoparticles with a worse dispersion have hydrophobic surface character due to the lack of amine groups on their surface.

#### 4. Conclusion

The XRD diffractogram pattern of the prepared  $\text{Fe}_3\text{O}_4/\text{C}$  showed main peaks characteristic peaks of C graphite and  $\text{Fe}_3\text{O}_4$  at  $2\theta$   $26.5238^\circ$  and  $35.6374^\circ$ , respectively. SEM and TEM analysis showed that the nanoparticle had a spherical morphology and that the structure of the nanoparticle was  $\text{Fe}_3\text{O}_4$  coated with carbon layers. The amine-modified  $\text{Fe}_3\text{O}_4/\text{C}$  had a better dispersion in the aqueous liquid medium than  $\text{Fe}_3\text{O}_4/\text{C}$ , indicating the ethylenediamine addition into the liquid medium during submerged arc discharge successfully modified the particles, producing hydrophilic surfaces.

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