

# Quantitative analysis by UV-Vis absorption spectroscopy of amino groups attached to the surface of carbon-based nanoparticles

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**Abstract.** Carbon-based nanoparticles must be modified due to their wide array of applications, especially when they are used as biomaterials. After modifying, quantitative analysis of the functional group is essential to evaluate a number of the available functional groups applied for further functionalization. In this study, we modified the carbon-based nanoparticles by amino group using submerged arc discharge in different liquids. The attached amino groups were then characterised and quantified by UV-Vis spectroscopy. This amino group functionalization was also confirmed by Fourier transform infrared (FTIR) spectra. The FTIR spectra of amine-modified nanoparticles show the definitive absorption peaks of N—H amine, C—H, C=O, C—N and Fe—O at 3418.97; 3000–2850; 1700–1600; 1400–1100; and 480–550  $\text{cm}^{-1}$ , respectively. The amine groups have different performance signals between the amine-modified and unmodified nanoparticles. The FTIR spectra results were correlated with the UV-Vis absorption spectroscopy method using acidic methyl orange. The UV-Vis absorption spectroscopy shows that the absorbance of methyl orange represented to amino groups number was 1.3 times higher when the pH of the solution was increased. The absorbance intensity was then used to estimate the quantity of amine groups attached.

## 1. Introduction

$\text{Fe}_3\text{O}_4$  materials have been studied in multiple reports due to their several phases such as ferromagnetic magnetite ( $\text{Fe}_3\text{O}_4$ ), maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) and hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) [1,2]. Furthermore, iron magnetic nanoparticles can be synthesised by various methods, such as electron beam irradiation methods, coprecipitation methods and emulsion precipitation methods [3-5]. The iron nanoparticles are also coated using other carbon materials to increase the absorption ability of the nanoparticles. Moreover, carbon coating can be used as an adhesion point for functional groups.

The magnetic-based nanocarbon material can also be synthesised by the arc discharge method. In the conventional arc discharge method, the vacuum pump and gas flow can be replaced using a liquid medium become a simple, easy and economical arc discharge method [6]. According to Sano et al. (2010), the arc discharge methods in the liquid produce nanomaterial products with high yield and lower impurities [7,8].



We previously reported the changing of the hydrophobic property of the carbon surface of  $\text{TiO}_2/\text{C}$  photocatalysts being hydrophilic during submerged arc discharge by using ethanol liquid with ethylenediamine or urea added [9,10]. One of the successful surface modifications of  $\text{TiO}_2/\text{C}$  with  $\text{NH}_2$  groups was performed in the medium of ethanol:ethylenediamine (1:1 v/v) and qualitatively analysed by N—H and C—N peaks shown in its Fourier transform infra-red (FTIR) spectrum [10]. However, a quantitative study has not yet been performed. Therefore, this study merged FTIR characterisation and chemical derivatization analysis using UV spectroscopy techniques to qualitatively and quantitatively examine the successful surface modification of amine groups attached to the  $\text{Fe}_3\text{O}_4/\text{carbon}$  nanoparticles prepared by submerged arc discharge using the ethanol/ethylenediamine medium.

## 2. Experimental details

### 2.1. Fabrication of amine-modified nanoparticles

Amine-modified nanoparticles were fabricated by the arc discharge method using carbon electrodes. The anode used was a carbon electrode filled with a mixture of carbon,  $\text{Fe}_3\text{O}_4$  and fructose binder with a weight ratio C: $\text{Fe}_3\text{O}_4$  of 3:1. Before filling, the mixture was sonicated for 480 s. After filling, the filled carbon electrodes were heated in a furnace at a temperature of  $180^\circ\text{C}$  for 6 h. The cathode was a sharp pencil-like graphite electrode, and the cathode and anode were positioned at a very close distance (less than 2 mm separation) to produce stepping electrons. Both the cathode and anode were submerged in a 600 mL glass beaker containing 300 mL ethanol 50%:ethylenediamine 50% (1:1 v/v). A current of 10 A ( $\sim 30$  V) then was passed through the electrodes, which causes arcing to occur. During this process, the nanomaterial was formed as a black powder dispersed in the liquid. For comparison, the arc discharge also was performed in a solution of only ethanol.

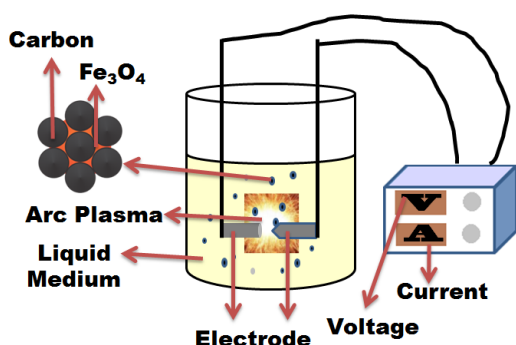
### 2.2. Characterizations of amine-modified nanoparticles

Black powder obtained from the previous section was characterised using FTIR instruments to qualitatively analyse the amine groups attached to the surface of the nanoparticles. The other analysis was performed by UV-Vis spectroscopy that followed the procedure in [11]. The amine-modified nanoparticles (0.005 g) were treated with 10 mL acidic methyl orange solution (0.05% methyl orange in a 0.1 M solution of sodium dihydrogen phosphate in water) for 2 minutes in a vortex mixer and then centrifuged at 8000 rpm for 5 minutes. After removing the excess dye by rinsing, the attached methyl orange was resolved by 5 mL of a 0.1 M potassium carbonate solution. The filtrate separated by centrifugation was then tested using UV-Vis absorption spectroscopy to quantitatively analyse the amine groups attached on the nanoparticle surfaces at a wavelength of 464 nm. The molar extinction coefficient of the methyl orange was  $\varepsilon = 21600 \text{ L}/(\text{mol cm})$ .

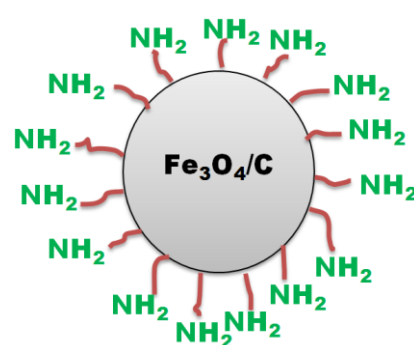
## 3. Results and discussion

The modified  $\text{Fe}_3\text{O}_4$  nanocomposite with carbon was successfully fabricated by using the arc discharge method in a liquid media of ethanol/ethylenediamine. Thus, the material product comprised amine-modified nanoparticles.

During arc discharging, a section of the tip of the filled carbon electrodes submerged in liquid was destructed and then evaporated in the arc area. The carbon vapour that moved away from the arc area then condensed on the  $\text{Fe}_3\text{O}_4$  particle, resulting in carbon encapsulated iron oxide ( $\text{Fe}_3\text{O}_4/\text{C}$ ) nanoparticles, which are illustrated in Figure 1. During the carbon layer condensation, the amine group from the ethylenediamine liquid was attached, covalently linked to  $\text{sp}^3$  carbon atoms. The ethyl group possibly helped the hexagonal based structure carbon to further form as graphite layers. The amine functional groups attached on the surface were responsible for the dispersion quality of  $\text{Fe}_3\text{O}_4/\text{C}$  in water, and the modified nanoparticle surface with the amine group is illustrated in Figure 2.

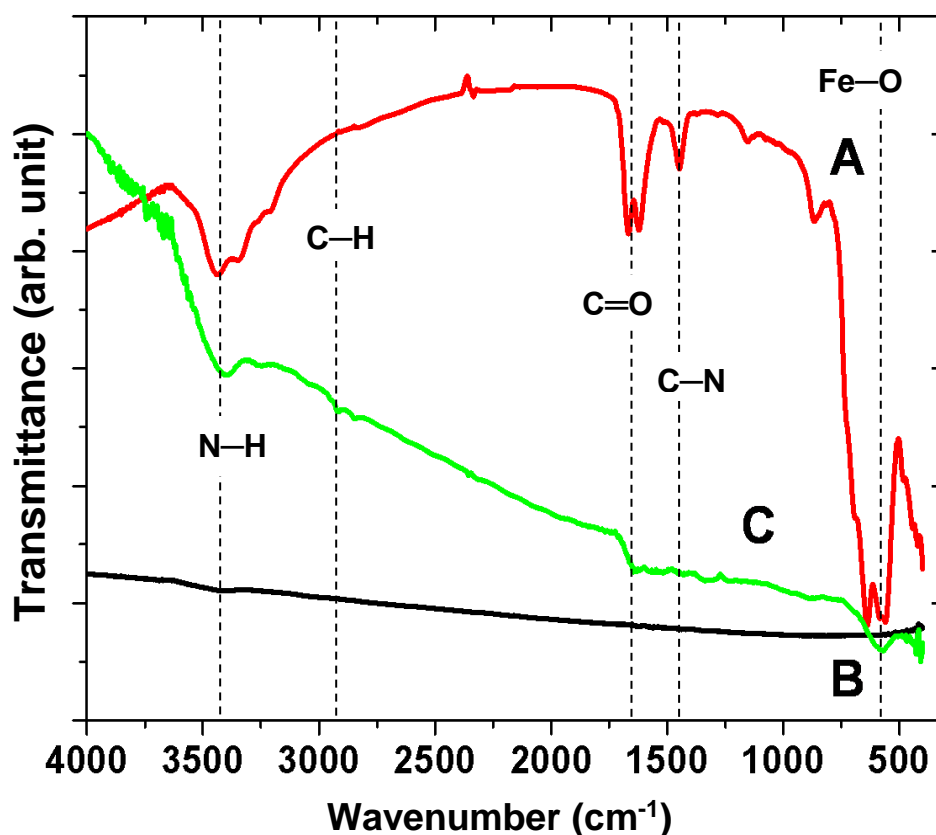


**Figure 1.** Illustration of arc discharging in liquid to form  $\text{Fe}_3\text{O}_4/\text{C}$  nanoparticles



**Figure 2.** Illustration of amine group modified  $\text{Fe}_3\text{O}_4/\text{C}$  nanoparticles

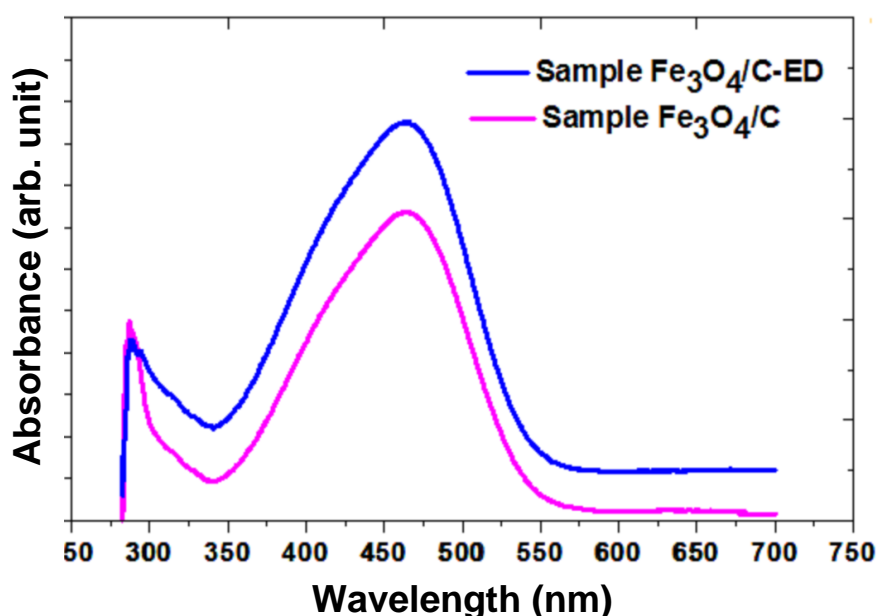
To characterise the presence of nitrogen-containing functional groups, FTIR characterisation was performed to identify the successful attachment of amine groups on the nanoparticle surface. The FTIR characterisation shown in the spectra in Figure 3 confirmed that the studied method synthesised  $\text{Fe}_3\text{O}_4/\text{C}$  functionalized amine groups. The figure revealed the transmittance of N—H amine, C—H, C=O, C—N and Fe—O at 3418.97; 3000–2850; 1700–1600; 1400–1100; and 480–550  $\text{cm}^{-1}$ , respectively.



**Figure 3.** FTIR spectra: iron oxide ( $\text{Fe}_3\text{O}_4$ ) (A), graphite powder (B), and amine-functionalized  $\text{Fe}_3\text{O}_4\text{-C}$  (C)

The presence of the N–H amine indicates the successful surface modification of  $\text{Fe}_3\text{O}_4/\text{C}$  nanoparticles by amine groups provided from the breakdown of the liquid medium of ethanol and ethylenediamine during the arc discharge process. The changes of surface characteristics of the particle due to the addition of a functional group derived from the liquid medium when synthesised in plasma arc discharge is illustrated in Figure 2. The amine groups were attached on the carbon layer via covalent bonds, and the covalent bonds were linked with carbon atoms in the hexagonal structure of graphite with the nitrogen atom of  $\text{NH}_2$ .

To quantitatively analyse the amine groups on the nanoparticle surfaces, the chemical derivatization of amine group was performed by a UV-Vis spectrometer using an acidic methyl orange (MO) solution. MO covalently bonds to the amine groups in the lower pH, and the bound MOs were released when the solution was in higher pH controlled by the potassium carbonate addition. The released MOs were easily detected by UV-Vis spectroscopy.



**Figure 4.** The UV-Vis absorption spectroscopy of acidic methyl orange released from  $\text{Fe}_3\text{O}_4/\text{C}$  and  $\text{Fe}_3\text{O}_4/\text{C-ED}$

Figure 4 shows the spectra of the MO released from the modified and unmodified nanoparticles. The spectra in the figure show that the absorption peak of MO was significantly different between two of those samples. The MO absorbance of amine-modified nanoparticles was 1.3 times higher than that of unmodified nanoparticles. Consequently, the amine group concentration presented on  $\text{Fe}_3\text{O}_4/\text{C-ED}$  was equal to  $0.022 \times 10^{-3}$  mol  $\text{NH}_2$  per one gram nanoparticles or  $0.13 \times 10^{20}$   $\text{NH}_2$  groups per one gram nanoparticles, if the initial value is multiplied by Avogadro's number.

#### 4. Conclusion

The amine group being attached on the surface of the nanoparticles was successfully confirmed by FTIR analysis and UV-Vis spectroscopy techniques. The FTIR spectra of  $\text{Fe}_3\text{O}_4/\text{C}$  synthesised in the liquid medium ethanol/ethylenediamine revealed transmission peaks representing N–H amine, C–H, C=O, C–N and Fe–O at 3418.97; 3000–2850; 1700–1600; 1400–1100; and 480–550  $\text{cm}^{-1}$ , respectively. The UV-Vis absorption spectroscopy technique shows that the peak of  $\text{Fe}_3\text{O}_4/\text{C}$  produced in the arc discharge in ethanol/ethylenediamine was 1.3 times higher than the peak of  $\text{Fe}_3\text{O}_4/\text{C}$  produced in only ethanol.

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