The Modification of Carbon with Iron Oxide Synthesized in Electrolysis Using the Arc Discharge Method

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Abstract. The modification of carbon-based nanomaterials with metals is widely studied due to its unique properties. Here, the modification of carbon nanomaterial with iron oxide has been successfully carried out. This modification was achieved using arc discharge in 50\% ethanol liquid media. The anode used in the arc discharge was prepared from a mixture of carbon and iron oxide that was synthesized in electrolysis and was then calcined at 250\°C with silicon binder with a mass ratio of 3:1:1, and the cathode used was graphite rod. Both electrodes were set in the nearest gap that could provide an arc during arc-discharging, leading to carbon-based nanoparticle formation. The diffractogram pattern of the X-ray diffraction of the fabricated nanoparticles confirmed the typical peak of carbon, iron oxide and iron. The magnetization value of the result analysis of the vibrating sample magnetometer was 9.9 emu/g. The bandgap energy measurement using diffuse reflectance ultra violet was estimated to be 2.18 eV. Using the transmission electron microscopy, the structure of the nanomaterial produced was observed as carbon-encapsulated iron compound nanoparticles.

1. Introduction
Carbon-based nanomaterials have a large surface area that can bind biomolecules with high capacity [1-4]. Carbon nanomaterials with graphite structures might also be used as protective shells or coatings on the outside of magnetic nanoparticles to prevent these nanoparticles from being rapidly oxidized, and the carbon layers also magnetically isolate the nanoparticles from each other [5].

At present, graphite-encapsulated magnetic nanoparticles [6-10] are promising candidate materials for drug delivery. The carbon or graphite layers can not only prevent iron nanoparticles from being rapidly oxidized but also magnetically isolate the nanoparticles from each other [5]. Graphite-encapsulated magnetic nanoparticles are conventionally prepared using the conventional arc-discharge method, which is conducted in low pressure using a sophisticated vacuum system. Two graphite electrodes are installed vertically, and the distance between the two rod tips is usually in the range of 1–2 mm. The anode and cathode are made of pure graphite (with a purity of 99.999\%). After evacuating the chamber with a vacuum pump, an appropriate ambient gas is introduced at the desired pressure. When a direct current (DC) arc voltage is applied between the two graphite rods, the anode is...
consumed and carbon-based nanoparticles are formed in the chamber soot [11]. Arc discharge has been used by Huffman and Krätschmer to prepare fullerene by evaporating graphite electrodes via restrictive heating in a helium atmosphere [12].

The conventional arc plasma growth method for carbon materials requires complex gas-handling equipment, a sealed reaction chamber, a liquid-cooled system and time-consuming purge cycles. Ishigami et al. developed a simple arc method in liquid nitrogen for high-quality carbon nanotube (CNT) synthesis [13]. Following this work, researchers generated carbon onions, nanotubes and encapsulates using arc discharge in water [14-17].

Here, we fabricated carbon-modified iron compound magnetic nanoparticles using arc discharge in a liquid medium of 50% ethanol as carbon sources using carbon electrodes and iron oxide-containing carbon electrodes. The iron oxide could be prepared using various methods. One of the easiest iron oxide preparation methods is the electrolysis method, which is a simple and economical process.

2. Experimental

2.1. Fabrication of iron oxide/carbon

The fabrication of carbon modified with iron oxide material was performed using the submerged arc discharge method. This method used two electrodes as the cathode and anode. The anode was a carbon electrode filled with a mix of graphite carbon, iron oxide (synthesized via electrolysis) and silica binder with a mass ratio composition of 3:1:1. The mix was sonicated for 480 seconds and then moulded into a rod with dimension of Ø 10 mm x 50 mm. The electrode was then heated in furnace at 180°C for 6 hours. The cathode used was a graphite electrode that had a sharp pencil tip. The cathode and anode distance were set with a very close gap to procure stepping electrons. Both the cathode and anode were set up in a 600-mL glass beaker containing 300 mL of 50% ethanol. A current of 10 A (13.75 V) was passed through electrodes. After arcing, the nanoparticles were collected, and the remaining ethanol was evaporated and dried.

2.2. Characterizations of iron oxide/carbon

The nanoparticles obtained from the arc discharge were characterized using an X-Ray Diffractometer (XRD-6000, Shimadzu) (Cu; 40.0 kV; 30.0 mA) to analyse the crystallinity and elements contained in the material. The magnetization of the material was measured using a vibrating sample magnetometer (VSM OXFORD type 1.2H). The change of band gap energy was determined using a diffuse reflectance spectrophotometer-ultra violet (UV 1700 PHARMASPEC). The structure, shape and size of the nanoparticle were studied using a transmission electron microscope (JEOL JEM-1400).

3. Result and Discussion

The nanoparticles synthesized by the submerged arc discharge were collected and named iron oxide/carbon. Fig. 1 shows a diffractogram of the iron oxide/carbon fabricated by arc discharge compared with the starting material of iron oxide synthesized via electrolysis and calcined at 250°C.

The X-ray diffraction (XRD) pattern of the initial material of iron oxide shown in Fig. 1(a) had agreement peaks to the Joint Committee on Powder Diffraction Standards (JCPDS) Fe₃O₄ or magnetite No. 89-0691 of magnetite Fe₃O₄. Some relevant peaks at 30,5296°; 35,9186°; 43,6172°; 53,9676°; 57,5602° and 74,6690° represented to the Fe₃O₄ planes of (220), (311), (400), (422), (511), and (440), respectively. After arcing as shown in Fig. 1(b), the existence of carbon peak on 26.5° represented to a graphitic layer of (002) and Fe₃O₄ peaks as mentioned are still confirmed. Moreover, several peaks at 20 = 26.5303°, 35,6197°, 43,1364°, 54,5446° and 77,387°, which, according to Joint Committee on Powder Diffraction Standards (JCPDS), matched Fe₃C No. 85-0871 on hkl (002) 26.50°, hkl (020) 35.598°, hkl (022) 43.23°, hkl (220) 54.57° and graphite JCPDS No. 41-1587 on hkl (110) 77.24°.

These distinguish peaks strengthen that during arc discharging, the incorporated structures of the starting material of iron oxide and carbon was successfully condensed in the plasma zone indicationg
that the product of this arc discharge is incorporated nanoparticles contained iron- and carbon-containing compounds.

Figure 1. Diffractogram of iron oxide (a) and iron oxide/carbon (b)

Figure 2. Hysteresis loop of iron oxide starting material (a) and iron oxide/carbon (b) fabricated by arc discharge.

Analysis was performed using the VSM to determine the magnetic properties of the material. Fig. 2 shows that the difference related to spin magnetization is irregular, which was caused by both the interaction of the superexchange between the Fe ions that were linked by O$^{2-}$ ions (Fe$^{3+}$-O$^{2-}$-Fe$^{3+}$) and the coordination between atoms, which is incomplete on the surface [18]. This phenomenon caused the magnetization of the iron oxide/carbon nanoparticles to be weaker than that of the iron oxide starting material. Moreover, the addition of carbon to the iron oxide nanoparticles caused the magnetization to
decrease. According to the hysteresis loop as shown in Fig. 2, both iron oxide and iron oxide/carbon have a superparamagnetic property with a magnetization value of 9.9 emu/g.

Fig. 3 shows the transmission electron microscopy (TEM) imaging of the iron oxide (Fig. 3(a)) and nanoparticle product of iron oxide/carbon (Fig. 3(b)). As shown in Fig. 3, the iron oxide particles had a diameter in the range of 30–40 nm and the nanoparticle product of iron oxide/carbon had a diameter in the range of 20–25 nm. The significant structures were clearly shown between both. The iron oxide was typically in a sphere without a coated layer, and the iron oxide/carbon had a core–shell structure. The core was highly probably occupied by iron oxide or iron carbide, and the shell was constructed from a carbon graphite layer.

![Figure 3](image)

**Figure 3.** The transmission electron microscope images (a) iron oxide and (b) iron oxide/carbon

For additional characterisation, the optical property of nanoparticle product was also studied. Table 1 shows the band gap energy of the iron oxide and iron oxide/carbon. The addition of carbon to the iron oxide material caused the band gap energy to decrease slightly from 2.25 eV to 2.18 eV. Since the nanoparticle product still had a similar band gap energy value, the carbon did not disturb the iron oxide structure; therefore, the iron oxide/carbon still had the same character as a semiconductor material as before.

| Materials           | Bandgap Energy (eV) |
|---------------------|---------------------|
| Iron oxide          | 2.25                |
| Iron oxide/carbon   | 2.18                |

**Table 1.** Bandgap energy of iron oxide and iron oxide/carbon fabricated by arc discharge.

4. **Conclusion**
The character of the product of iron oxide/carbon prepared by submerged arc discharge has a crystalline structure with distinctive peaks representative of iron oxide, graphite, and a new peak of iron carbide. The nanoparticle had a nanosize and superparamagnetic property with a magnetization value of 9.9 emu/g. The bandgap energy of the iron oxide/carbon narrowed from 2.25 eV to 2.18 eV. The structure of nanoparticle product was observed as a core–shell structure with an iron compound core coated by a carbon shell.

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