Influence of TiO$_2$ addition on the magnetic properties of carbon-based iron oxide nanocomposites synthesized using submerged arc-discharge

Diah Ayu Rivani$^1$, Indah Retnosari$^1$, Kusumandari$^2$, Teguh Endah Saraswati$^1$

$^1$ Department of Chemistry, Faculty of Mathematics and Natural Sciences
$^2$ Department of Physics, Faculty of Mathematics and Natural Sciences Sebelas Maret University, Ir. Sutami 36A Surakarta, 57126 Indonesia

* Corresponding author: teguh@nipa.uns.ac.id

Abstract. The influence of TiO$_2$ addition on the magnetic properties of Fe$_3$O$_4$ and carbon nanocomposites was studied. The nanocomposites were synthesized using a one-step submerged arc-discharge method in a liquid medium of 50% ethanol solution using two carbon electrodes. The magnetic properties of the resulting materials were characterized using a Vibrating Sample Magnetometer (VSM). The changes in the crystalline structures were studied using X-ray Diffraction (XRD). We confirmed that TiO$_2$ addition caused no changes in magnetite phase Fe$_3$O$_4$. Several intense peaks in the XRD diffractogram at 2θ: 35.5, 43.1 and 57° corresponded to diffractions Fe$_3$O$_4$ magnetite planes of (311), (400) and (511), respectively. The hysteresis pattern of the magnetic properties analysed by VSM showed that the addition of TiO$_2$ did not affect their superparamagnetic character. However, the TiO$_2$/Fe$_3$O$_4$/C nanocomposites had higher saturated magnetization ($M_s$) than the Fe$_3$O$_4$/C nanocomposites without TiO$_2$ addition.

1. Introduction

Magnetic nanocomposites are materials of interest for study and development because they have a variety of potential applications in various fields—for example, for magnetic storage, bioimaging, biosensor and drug delivery applications [1-6]. This is because magnetic nanocomposite materials have different chemical and physical properties [7]. One example of a magnetic material is Fe$_3$O$_4$ magnetite, which could be used in the environmental field for the degradation of wastewater, especially dye wastewater, when combined with a photocatalyst material (TiO$_2$) [8].

Fe$_3$O$_4$ is one of the iron oxides other than maghemite (γ-Fe$_2$O$_3$) and hematite (α-Fe$_2$O$_3$); it is a more powerful magnetic material than other iron oxides [9]. Magnetite (Fe$_3$O$_4$) has an inverse cubic spinel structure [10]. The crystal structure of Fe$_3$O$_4$ consists of a unit cell which contains oxygen ions in close-packed (face-centred cubic) FCC structure and iron ions that form the tetrahedral and octahedral structures, represented by $[\text{Fe}^{3+}]_4$ $[\text{Fe}^{2+}\text{Fe}^{3+}]_8\text{O}_16$, in which the tetrahedral position is occupied by Fe$^{3+}$ ions and the octahedral position is occupied by eight Fe$^{3+}$ and eight Fe$^{2+}$ ions, as shown in figure 1 [11, 12].

Carbon-based magnetic nanocomposites have also received attention due to their beneficial properties. Carbon is a non-metallic element with interesting properties such as a high surface area and a porous structure [13]. Carbon forms multiple allotropes, which come in crystalline carbon and non-crystalline forms. Examples of crystalline carbon include graphite, diamond and fullerene, while non-crystalline carbon includes amorphous and activated carbon [14, 15]. Incorporating carbon material with
magnetic iron oxide makes the magnetic nanocomposite more stable because it can prevent further metal and/or metal oxide oxidation. Moreover, the carbon layer is suitable for surface functionalization with the other molecules due to its greater surface area, making it more easily modifiable [16].

![Figure 1. The inverse spinel structure of magnetite Fe₃O₄.](image)

Meanwhile, titanium dioxide (TiO₂) is the most effective semiconductor photocatalyst because it has a relatively large energy gap of 3.2 eV, which is suitable for photocatalysts, and it is non-toxic, cheap and abundant in nature [17-19]. TiO₂ has three phases of crystal structure—anatase, rutile and brookite [17, 20]. However, only the anatase and rutile phases are stable enough, whilst the brookite crystalline phase may change at elevated temperatures [20, 21].

Taking into account the physical and chemical properties of TiO₂, Fe₃O₄ and carbon materials, their combination is interesting to examine. There are several method reported for producing their combination such as sol-gel [8, 22, 23], co-precipitation [24], hydrothermal [25], Saraswati et al. [26], Saraswati et al. [27] and Arikawati and Saraswati [28] conducted coupling of TiO₂ with carbon using arc-discharge in a liquid medium [26-29]. This method is simple, low-cost and efficient in producing combined nanomaterials.

In this study, the addition of TiO₂ to an Fe₃O₄/carbon nanocomposite was performed using the arc-discharge method. The changes in the physical and chemical properties of the resultant material are interesting to study, as they affect its role in a particular application. Therefore, this article will discuss the crystallinity and magnetic properties of Fe₃O₄/C nanocomposites with and without the addition of TiO₂ nanoparticles, synthesized using the arc-discharge method in ethanol-based liquid media.

2. Experimental Details

2.1. Materials
The materials used were 50% ethanol solution, distilled water, Fe₃O₄ (prepared by electrolysis), TiO₂ (technical grade, Bratachem, Indonesia), carbon electrodes from Qingdao Tenry Carbo Co. Ltd (Carbon 99%; density 1.95 g/cm³; electrical resistance 7-10 ohm; dimension of d_inner=7 mm, d_outer=10 mm; length=50 mm), graphite (Merck) and fructose (Rose Brand).

2.2. Synthesis of Nanocomposite TiO₂/Fe₃O₄/C.
A graphite electrode was filled with a mixture of TiO₂ anatase, Fe₃O₄ powder, carbon powder and fructose as a binder in a weight ratio of 1:1:3:2 for nanocomposite TiO₂/Fe₃O₄/C production, while for the preparation of the Fe₃O₄/C nanocomposite, a graphite electrode was filled with a mixture of Fe₃O₄ powder and carbon powder with fructose as binder in a weight ratio of 1:3:2. The electrode was heated at a temperature of 180°C for 6 hours. The liquid medium consisted of 300 ml of 50% ethanol solution.

Two graphite electrodes, an unfilled carbon electrode and filled carbon electrode, were set in the liquid medium at a very close distance. The synthesis process was conducted by passing a voltage of 20 V and current of 10 A between them. The resulting nanocomposites were collected from the surface and bottom
of the liquid medium. The collected TiO$_2$/Fe$_3$O$_4$/C nanocomposite was characterized using X-Ray Diffraction (XRD) Bruker DS to determine the crystallinity and crystal structure. A Vibration Sample Magnetometer (VSM) was used to determine the magnetic properties of the materials at room temperature.

3. Results and Discussion

After the synthesis process, the products were characterised to confirm their properties. The crystallinity of the synthesized TiO$_2$/Fe$_3$O$_4$/C nanocomposite was analysed using XRD, as shown in figure 2. The resulting diffractogram shows the peaks of the starting materials of the Fe$_3$O$_4$ nanomaterials that appear at 2$\theta$: 35.1° hkl (311), 43.1 hkl (400) and 57° hkl (511); JCPDS No. 88-0315. The peak representing carbon appears at 2$\theta$: 26.3° hkl (002); JCPDS No. 41-1487. Products with TiO$_2$ addition displayed peaks representing TiO$_2$ at 2$\theta$: 25.28° hkl (101), 48.21 hkl (200), 54.08° hkl (105) and 62.70° hkl (204); JCPDS No. 86-1157. The emergence of a new peak for titanium carbide (TiC) was observed at 2$\theta$: 29.40 hkl (104); JCPDS No.22-2496. The formation of TiC was due to the reactions between TiO$_2$ and carbon as follows: TiO$_2$(s) + 3C(s) $\rightarrow$ 2CO(g) + TiC(s) [30].

![Figure 2. XRD profiles of TiO$_2$/Fe$_3$O$_4$/C (a) and Fe$_3$O$_4$/C (b) nanocomposites.](image)

The surface structure morphology of nanocomposites fabricated using arc-discharge was characterised by scanning electron microscopy (SEM) and EDX elemental analysis, as shown in figure 3 and table 1, respectively. The morphology shown by the SEM analysis of the Fe$_3$O$_4$/C and Fe$_3$O$_4$/TiO$_2$/C nanocomposites at a magnification of 15,000X was spherical and regular. As shown in the SEM images in figure 2, Fe$_3$O$_4$/C materials aggregated in a spherical and regular structure at a nanometre scale, where Fe$_3$O$_4$/C clusters had a smaller size than Fe$_3$O$_4$/TiO$_2$/C, forming microsphere aggregates. It can be concluded that the structural and morphological properties of the products of Fe$_3$O$_4$/C nanocomposites did not change regardless of the addition of TiO$_2$. 
Figure 3. SEM imaging of Fe₃O₄/C (left) and Fe₃O₄/TiO₂/C (right).

Based on the results of the EDX analysis shown in table 1, the C, O and Fe elements in the Fe₃O₄/C nanocomposite had weight percentages of 66.49%, 27.77% and 5.74%, respectively, while the percentages of C, O, Fe and Ti elements in the Fe₃O₄/TiO₂/C nanocomposite were 64.74%, 29.32%, 4.43%, and 1.50%. In the Fe₃O₄/C nanocomposite, about 2.033% of oxygen atoms bonded with iron to form Fe₃O₄; the remaining wt% of oxygen bonded to other atoms to form oxygen-containing functional groups attached to C elements, such as hydroxyl and carboxyl groups. In the Fe₃O₄/TiO₂/C nanocomposite, O bonded with Ti and Fe to form TiO₂ and Fe₃O₄, and to other atoms to form oxygen-containing functional groups and oxygen-containing compounds such as titanium oxide (TiₓOᵧ).

Table 1. EDX Elemental analysis of Fe₃O₄/C and Fe₃O₄/TiO₂/C.

| Elements | Wt% Fe₃O₄/C | Wt% Fe₃O₄/TiO₂/C |
|----------|-------------|-----------------|
| C        | 66.49       | 64.74           |
| O        | 27.77       | 29.32           |
| Fe       | 5.34        | 4.43            |
| Ti       | -           | 1.50            |
| Total    | 100.00      | 100.00          |

The magnetic properties were then further characterised using VSM. The saturated magnetization (Mₛ) and coercive magnetic field (Hₖ) are shown in table 2. Compared to TiO₂, Fe₃O₄ has greater magnetic properties. Fe₃O₄ has a magnetic moment of 28 μB [31], while TiO₂ and C have zero magnetic moment [32-34]. Therefore, the magnetic moment depends on the presence and the crystalline structure of Fe₃O₄.

Table 2. Values of VSM test analysis on Fe₃O₄/C and TiO₂/Fe₃O₄/C nanocomposites.

| Sample         | Mₛ (emu/gr) | Hₖ (T)   |
|----------------|-------------|----------|
| Fe₃O₄/C        | 10.4705     | 0.00931  |
| TiO₂/Fe₃O₄/C  | 12.5936     | 0.00516  |

As shown in table 2, the TiO₂/Fe₃O₄/C nanocomposite had a slightly stronger Mₛ than the Fe₃O₄/C nanocomposite. The Mₛ of products with TiO₂ addition increased 20% from that of products without TiO₂ addition. Due to their smaller size, carbon atoms were interstitially allowable, entering into the
crystal cavity of the metal oxide [31, 34]. However, the carbon atoms interacted more with TiO$_2$ due to the wider cavity size of TiO$_2$ compared to that of Fe$_3$O$_4$, as shown in figure 4. Therefore, the magnetization in TiO$_2$/Fe$_3$O$_4$/C was higher because there was less carbon interference in Fe$_3$O$_4$ crystals than in Fe$_3$O$_4$/C.

![Figure 4](image_url)

**Figure 4.** The crystalline structure of Fe$_3$O$_4$ (a) and TiO$_2$ (b).

In addition, the H$_c$ of both materials was close to zero, indicating that the superparamagnetic property of the material products was maintained [35]. The preferable interaction induced a carbothermal reduction reaction between TiO$_2$ and C, as evidenced by the appearance of a new TiC material peak after the addition of TiO$_2$, which agrees with the XRD spectra shown in figure 1.

4. Conclusion
The synthesis of Fe$_3$O$_4$/C and TiO$_2$/Fe$_3$O$_4$/C nanocomposites was performed using the arc-discharge method in 50% ethanol liquid media. According to the VSM results, the saturated magnetization of the TiO$_2$/Fe$_3$O$_4$/C nanocomposite is greater than that of the Fe$_3$O$_4$/C nanocomposite because the carbon atoms more easily interfered with the TiO$_2$ crystalline structure than that of Fe$_3$O$_4$. However, the superparamagnetic properties of both materials were maintained.

Acknowledgments
This work was partially supported by Grants-in-Aid of Research from the Ministry of Research, Technology and Higher Education under project No. 474/UN27.21/PP/2018.

References
[1] Zhu K, Ju Y, Xu J, Yang Z, Gao S and Hou Y 2018 Magnetic Nanomaterials: Chemical Design, Synthesis, and Potential Applications Acc. Chem. Res. 51 2 404-13
[2] Bagheri S and Julkapli N M 2016 Modified iron oxide nanomaterials: Functionalization and application J. Magn. Magn. Mater. 416 117-33
[3] Veiseh O, Gunn J W and Zhang M 2010 Design and fabrication of magnetic nanoparticles for targeted drug delivery and imaging Adv. Drug Deliv. Rev. 62 3 284-304
[4] Chomoucka J, Drbohlavova J, Huska D, Adam V, Kizek R and Hubalek J 2010 Magnetic nanoparticles and targeted drug delivering Pharmacol. Res. 62 2 144-9
[5] Frey N A, Peng S, Cheng K and Sun S 2009 Magnetic nanoparticles: synthesis, functionalization, and applications in bioimaging and magnetic energy storage Chem. Soc. Rev. 38 9 2532-42
[6] Sun C, Lee J S and Zhang M 2008 Magnetic nanoparticles in MR imaging and drug delivery Adv. Drug Deliv. Rev. 60 11 1252-65
[7] Akbarzadeh A, Samiei M and Davaran S 2012 Magnetic nanoparticles: preparation, physical properties, and applications in biomedicine Nanoscale Res. Lett. 7 1 144
[8] Li Y, Zhang M, Guo M and Wang X 2009 Preparation and properties of a nano TiO 2/Fe 3 O 4
composite superparamagnetic photocatalyst Rare Metals 28 5 423-7

[9] Cornell R M and Schwertmann U 2003 The iron oxides: structure, properties, reactions, occurrences and uses: John Wiley & Sons)

[10] Teja A S and Koh P-Y 2009 Synthesis, properties, and applications of magnetic iron oxide nanoparticles Prog. Cryst. Growth Charact. Mater. 55 1-2 22-45

[11] Mazo-Zuluaga J, Restrepo J and Mejia-López J 2007 Surface anisotropy of a Fe3O4 nanoparticle: A simulation approach Physica B Condens. Matter 398 2 187-90

[12] Taimoory S M, Trant J F, Rahdar A, Aliahmad M, Sadeghfar F and Hashemzaei M 2017 Importance of the inter-electrode distance for the electrochemical synthesis of magnetite nanoparticles: Synthesis, characterization, computational modelling, and cytotoxicity E J. Surf. Sci. Nanotechnol. 15 31-9

[13] Shornikova O, Kogan E, Sorokina N and Avdeev V 2009 The specific surface area and porous structure of graphite materials Russ. J. Phys. Chem. A 83 6 1022-5

[14] Hirsch A 2010 The era of carbon allotropes Nat. Mater. 9 11 868

[15] Falcao E H and Wudl F 2007 Carbon allotropes: beyond graphite and diamond J. Chem. Technol. Biotecnol. Int. Res. Process Environ. Clean Technol. 82 6 524-31

[16] Saraswati T E, Ogino A and Nagatsu M 2012 Plasma-activated immobilization of biomolecules onto graphite-encapsulated magnetic nanoparticles Carbon 50 3 1253-61

[17] Linsebigler A L, Lu G and Yates Jr J T 1995 Photocatalysis on TiO2 surfaces: principles, mechanisms, and selected results Chem. Rev. 95 3 735-58

[18] Nakata K and Fujishima A 2012 TiO2 photocatalysis: Design and applications J. Photochem. Photobiol. C Photochem. Rev. 13 3 169-89

[19] Fujishima A, Zhang X and Tryk D A 2008 TiO2 photocatalysis and related surface phenomena Surf. Sci. Rep. 63 12 515-82

[20] Reyes-Coronado D, Rodríguez-Gattorno G, Espinosa-Pesqueira M, Cab C, de Coss R d and Oskam G 2008 Phase-pure TiO2 nanoparticles: anatase, brookite and rutile Nanotechnology 19 14 145605

[21] Xiao Q, Zhang J, Xiao C, Si Z and Tan X 2008 Solar photocatalytic degradation of methylene blue in carbon-doped TiO2 nanoparticles suspension Sol. Energy 82 8 706-13

[22] Stefan M, Pana O, Leostean C, Bele C, Silipas D, Senila M and Gautron E 2014 Synthesis and characterization of Fe3O4–TiO2 core–shell nanoparticles J. Appl. Phys. 116 11 114312

[23] Ahmed M, El-Katori E E and Gharni Z H 2013 Photocatalytic degradation of methylene blue dye using Fe2O3/TiO2 nanoparticles prepared by sol–gel method J. Alloys Compd. 553 19-29

[24] Khashan S, Dagher S, Tit N, Alazzam A and Obaidat I 2017 Novel method for synthesis of Fe3O4@TiO2 core–shell nanoparticles Surf. Coat. Technol. 322 92-8

[25] Tan L, Zhang X, Liu Q, Jing X, Liu J, Song D, Hu S, Liu L and Wang J 2015 Synthesis of Fe3O4@TiO2 core–shell magnetic composites for highly efficient sorption of uranium (VI) Colloids Surf. A Physicochem. Eng. Asp. 469 279-86

[26] Saraswati T E, Andhika I F, Nandika A O, Wahyuningsih S and Purnawana C 2015 Synthesis and Surface Modification of TiO2/Carbon Photocatalyst Produced by Arc Discharge in Ethanol Medium The 9th Joint Conference on Chemistry

[27] Saraswati T E, Andhika I F, Purnawan C, Wahyuningsih S and Anwar M 2015 Photocatalytic Degradation of Methylene Blue Using TiO2/Carbon Nanoparticles Fabricated by Electrical Arc Discharge in Liquid Medium Adv. Mater. Res. 1123 285-8

[28] Ariyakwati E and Saraswati T E 2017 Preparation of Amine-Functionalized TiO2/Carbon Photocatalyst by Arc Discharge in Liquid IOP Conf. Ser. Mater. Sci. Eng. 176 1 012045

[29] Saraswati T, Nandika A, Andhika I, Purnawan C, Wahyuningsih S and Rahardjo S 2017 Fabrication of TiO2/Carbon Photocatalyst using Submerged DC Arc Discharged in Ethanol/Acetic Acid Medium IOP Conf. Ser. Mater. Sci. Eng. 202 1 012058

[30] Swift G and Koc R 1999 Formation studies of TiC from carbon coated TiO2 J. Mater. Sci. 34 13 3083-93
[31] Persson K 2015 Materials Data on Fe$_3$O$_4$ (SG:227) by Materials Project. United States
[32] Persson K 2014 Materials Data on C (SG:227) by Materials Project. (United States
[33] Persson K 2014 Materials Data on C (SG:194) by Materials Project. (United States
[34] Persson K 2014 Materials Data on TiO$_2$ (SG:141) by Materials Project. (United States
[35] Laurent S, Forge D, Port M, Roch A, Robic C, Vander Elst L and Muller R N 2008 Magnetic iron oxide nanoparticles: synthesis, stabilization, vectorization, physicochemical characterizations, and biological applications Chem. Rev. 108 6 2064-110