Synthesis and magnetic properties of graphene oxide-decorated cobalt, manganese and nickel ferrite nanoparticles prepared by polymerized route

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Abstract. Magnetic nanomaterials with emergent physical and chemical properties have paid much attention, however, their synthesis pathways are still a challenge. In this study, we described a simple method for the synthesis of graphene oxide-decorated magnetic nanoparticles GO@MFe₂O₄ (M = cobalt, manganese and nickel metal sites) from ferrites MFe₂O₄ via complex polymerization method and graphene oxide via Hummer’s method. The structure of GO@MFe₂O₄ were characterized by several physicochemical techniques, such as X-ray Diffraction (XRD) and Scanning electron microscope (SEM), Brunauer–Emmett–Teller (BET), point of zero charge (pHₚzc) and Fourier-transform infrared spectroscopy (FTIR). The results indicated a spinel-like structure of GO@MFe₂O₄ with high porosity and surface area, along with strong saturation magnetization, which can become a potential candidate for various applications.

1. Introduction

Magnetic nanomaterials (MNPs) possess a wide range of emergent physical and chemical properties in comparison with their precursor materials [1-3]. In particular, magnetic ferrite nanocrystals MFe₂O₄ (M = Co, Mn, Ni) have recently have recently paid much attention in various fields because of their remarkably sized and shape magnetic nanostructures [4-6].

Structurally, magnetic properties of ferrite nanocrystals MFe₂O₄ are mainly attributable the microstructure and cation distribution [7, 8]. Generally, in several normal spinels (e.g. MnFe₂O₄), tetrahedral A sites are occupied by divalent cations occupy, while octahedral B sites are occupied by trivalent cations [9]. Especially, both tetrahedral A and octahedral B interstitial sites are likely to be occupied by the cations in cubic spinel MFe₂O₄ structure [10]. These properties can be driven by a structural control of pore size and specific shape, therefore, making MNPs materials appropriate to potential applications from design of devices in biomedical sciences for protein separation, drug delivery, and cancer hyperthermia to magnetic resonance imaging (MRI) [11-13].
Several studies reported different methods to fabricate spinel MFe$_2$O$_4$, such as polymerized method, chemical co-precipitation, mechanical alloys, hydrothermal and solvothermal reactions, and sonochemical route [14, 15]. However, insight into a facile synthetic method for ferrite nanoparticles with well-controlled magnetic properties for various applications is still a challenge [10]. For example, Xia and Liu et al. reported that the use of CoFe$_2$O$_4$-graphene nanocomposites as a high-capacity anode material for lithium-ion batteries could be successfully synthesized by solvothermal method for the improvement of cycle performances [16].

Other strategies are restrained partly because of the use of toxic organic metal precursors, partly because of a prerequisite of the Ar or N$_2$ non-ambient atmosphere [13]. Meanwhile, complex polymerization method presents as an efficient route for the synthesis of MNPs with good chemical homogeneity [17]. This experimental procedure uses the simple, inexpensive, and rapid thermal decomposition approaches to obtain monodisperse nanoparticles. Moreover, for commercial perspective, complex polymerization method is an economic and scalable ‘greener’ approach to synthesis MNPs [13].

Recently, several substrates have been coated on nanoparticles MFe$_2$O$_4$ (M=Co, Ni, Mn) to obtain the desirable magnetic properties in biomedicine and bioengineering fields [4]. However, the requirements for these coating materials are low toxicity and high biocompatibility. Fe-based nanoparticles coated with graphene oxides (GO) were reported as non-toxic in human lymphocytes [18-20]. The presence of functional groups of graphene oxides are to increase the oxygen-containing adsorption sites with good stability, thus making them a suitable candidate for adsorption applications [21].

Graphene is constituted by two-dimensional sp$^2$-hybridized carbon single layers containing the hexagonal crystal structures. Meanwhile, graphene oxide derived from graphene via exfoliation with chemical oxidants such as H$_2$O$_2$, KMnO$_4$, H$_2$SO$_4$, and K$_2$S$_2$O$_8$. These carbonaceous compounds have exhibited several exceptional properties, playing a crucial role in dyes treatment because of its diverse kinds of nitrogen/oxygen-containing functional groups on surface, large surface area, and highly porous sites [22-26]. Combining between graphene oxide and MNPs aims to develop a form of nanocomposite with strong magnetism, increase the number of functional groups and decrease the agglomeration [27-29]. These materials might be therefore easy to perform magnetic separation and recycling in adsorption.

In this context, complex polymerization method was used to synthesize magnetic ferrite nanocrystals with cobalt, manganese and nickel oxide sites. The GO@MFe$_2$O$_4$ (M= Co, Mn, Ni) nanocomposites could be prepared using a two-step approach. The first step was to synthesize the MFe$_2$O$_4$ (M= Co, Mn, Ni) by complex polymerization method and graphene oxide by Hummers’ method. Next, these ferrite nanocrystals was combined with dispersed graphene oxide in the presence of ethanol solution via a procedure of temperature thermal decomposition (1000°C) to create the GO@CoFe$_2$O$_4$ MNPs. The samples were then characterized to show morphological, magnetic properties by several techniques such as SEM, IR, pH$_{pzc}$ and VSM.

2. Experiments

2.1. Chemicals and instruments
All chemicals including iron (III) chloride, cobalt (II) chloride, manganese (II) chloride and nickel (II) chloride, citric acid (93 g) and ethylene glycol were commercially purchased from Merck KGaA. All MNPs samples were pretreated to remove moisture at 100°C for 1 h before analyzing. The scanning electron microscope (SEM) was recorded by instrument S4800, Japan and used an accelerating voltage source of 15 kV with the magnification of 7000. An energy dispersive spectroscopy (EDS) analysis of the arrays, performed at 15 kV coupled to the field-emission scanning electron microscope. The magnetic properties were determined by Vibrating Sample Magnetometer (VSM). The FT–IR spectra were recorded by using the Nicolet 6700 spectrophotometer instrument. The N$_2$ adsorption/desorption
isotherm was obtained using the Micromeritics 2020 volumetric adsorption analyzer system, before analysis the MPC sample was degassed in a vacuum for 6 h at 150 °C.

2.2. Preparation of graphene oxide
Graphene oxide was synthesized by Hummer’s method, using the natural graphite powder exfoliated with the several oxidants [30]. In the typical experiment, 3.0 g graphite 3.0 g was added into a 500 mL flask containing 150 mL concentrated H$_2$SO$_4$ 98% placed an ice bath (3 °C -5 °C) under stirring. After that, 10.5 g KMnO$_4$ was slowly added for 20 min and stirred overnight at room temperature. Then, 250 mL of deionized water was poured into stirred mixture and followed by a slow addition of 5 mL H$_2$O$_2$ 30 wt% until obtained a golden yellow solution. The products were next washed with 1L HCl 3% and then 1 L deionized water for three times. The graphene oxide was suspended in distilled water and dialyzed with deionized water overnight to remove metal ions and acids.

2.3. Preparation of MFe$_2$O$_4$ (M= Co, Mn, Ni) by polymerized method
Magnetic nanoparticles MFe$_2$O$_4$ (M= Co, Mn, Ni) were prepared by the polymerized complex method (PC) [21]. A mixture of citric acid (93 g), 100 mL of deionized water and ethylene glycol (40 mL) were dissolved at 80 °C until obtaining a homogeneous solution. After adding another mixture of 0.36 g CoCl$_2$. 6H$_2$O or 0.303 g for MnCl$_2$. 6H$_2$O or 0.36 g for NiCl$_2$. 6H$_2$O and 0.5 g FeCl$_3$. 6H$_2$O, the solution was stirred for several hours at 130 °C to obtain a polymeric resin precursor. The black powder precursor could be obtained when heating the solid under air atmosphere at temperatures 1000 ºC for 2h.

2.4. Preparation of GO@MFe$_2$O$_4$ (M= Co, Mn, Ni) nanocomposites
The GO@MFe$_2$O$_4$ (M= Co, Mn, Ni) nanocomposites were prepared by two-step procedure [26]. In the typical experiment, 1.0 g MFe$_2$O$_4$ (M= Co, Mn, Ni) material was added into a beaker containing 50 mL C$_2$H$_5$OH and 5 mL of GO colloidal suspension in 45 mL of water. The beaker was put in an ultrasonic bath for 1h, and after heated to 60 °C until approaching a complete vapourization. The solid was dried at 100 °C and used for the next studies.

2.5. Determination of pH$_{pzc}$ (pH point of zero charges)
The procedure for pH$_{pzc}$ determination can be performed according to a previous report [21]. The GO@MFe$_2$O$_4$ (M= Co, Mn, Ni) nanocomposites (m$_b$ = 5.0 mg) was added a flask containing 25 mL of KCl 0.1 mol/L at the different pH 2, 4, 6, 8, 10, 12. Note that HCl and NaOH 1 mol/l were used to adjust the pH indexes. The mixture was stirred during 24 h, and then the solid was then separated. The solids were then separated from the mixture using magnetic and centrifugal methods, and their final pH$_2$ were measured by a pH meter. The curve was plotted via ΔpH = pH$_1$ – pH$_2$ versus pH$_1$ and the pH$_{pzc}$ was calculated at ΔpH = 0.

3. Results and discussion

3.1. SEM images of GO@MFe$_2$O$_4$ (M= Co, Mn, Ni)
Morphological patterns in Figure 1 compare the evidence agglomeration and close arrangement with a spinel-like surface, which is attributable due the strong effect of magnetic properties derived from initial ferrites MFe$_2$O$_4$ and the Vander Waals forces, creating the assembly among the primary particles. This observation can be consolidated by the change in agglomeration form of GO@MFe$_2$O$_4$ as seen from Figure 1. The accumulative state of MNPs is the strongest in the form of GO@CoFe$_2$O$_4$, and weakest in form of GO@MnFe$_2$O$_4$, which are well matched with their saturation magnetization values [31]. Otherwise, blurred white spots appears nanosheet spinel surface was attributable to the existence
of graphene oxides layers [32]. Otherwise, the average diameter of particles in Figure 1 also reveals a size distribution in the range from about 300 nm to 500 nm.

![Figure 1. SEM images of GO@CoFe₂O₄ (a-c), GO@MnFe₂O₄ (d-f), GO@NiFe₂O₄ (g-i).](image)

3.2. VSM curves of GO@MFe₂O₄ (M= Co, Mn, Ni)

The magnetization curves of GO@MFe₂O₄ (M= Co, Mn, Ni) can be plotted by using the VSM technique and shown in Figure 2. The saturation magnetization values were measured by the following trend: GO@MnFe₂O₄ (1.8 emu/g) < GO@NiFe₂O₄ (2.4 emu/g) < GO@CoFe₂O₄ (4.5 emu/g).

Although the saturation magnetization values of graphene oxide-decorated nanocomposites GO@MFe₂O₄ are so far lower than those of their ferrites MFe₂O₄, the magnetic strength of graphene oxide-decorated ferrite also obeys the order of respective graphene oxide-free ferrites as several previous reports: MnFe₂O₄ < NiFe₂O₄ < CoFe₂O₄ [33, 34]. The presence of non-magnetic graphene oxide layer coating on the surface of magnetic ferrites results in a decrease in magnetic nanoparticle coverage, making the magnetization density and saturation magnetization values fall down.

Obtaining the magnetization values is a significant characteristic of GO@MFe₂O₄ in several application fields, such as adsorption because the solid adsorbent can be easily separated by inducing a magnetic field (e.g., a magnet). Therefore, this feature can facilitate separation and recyclability processes.
Figure 2. The VSM curves of GO@MFe$_2$O$_4$.

3.3. FT-IR spectra of GO@MFe$_2$O$_4$ (M= Co, Mn, Ni)

Figure 3 shows the Fourier-transform infrared spectroscopy spectra of GO@MFe$_2$O$_4$ (M= Co, Mn, Ni) MNPs. The very typical frequency bands of GO@MFe$_2$O$_4$ at around 536, 530, and 590 cm$^{-1}$ wavelengths are attributable to Fe (III)–O in octahedral and tetrahedral sites and the bands at around 452, 440, and 433 cm$^{-1}$ wavelengths refer to Fe (II)–O vibrations in octahedral sites [35]. Several literatures indicated that these stretching vibrations at low frequency bands could be derived from the spinel ferrite phase of Fe$_3$O$_4$ MNPs while the Fe–O bands at around 530-590 cm$^{-1}$ is a typical band for γ-Fe$_2$O$_3$ uniform [13, 36].

Moreover, all spectra reveal the presence of several stretching vibrations in common, such as hydroxyl groups O-H at 3420-3442 cm$^{-1}$, which is likely to originate from adsorbed H$_2$O or carboxylic acid trace from graphene oxide exists on the surface after synthesis of GO@MFe$_2$O$_4$. In addition, carbonyl groups (e.g., ketones, aldehydes) C=O vibrations and C-H stretching of alcoholic/aromatic groups can be confirmed at 1626-1630 and 1364-1442 cm$^{-1}$, respectively [37].

Figure 3. FTIR spectra of GO@MFe$_2$O$_4$.

Figure 4. The pH$_{pzc}$ curves of GO@MFe$_2$O$_4$. 
3.4. pH_{pzc} plots of GO@MFe_{2}O_{4} (M= Co, Mn, Ni)

The point of zero charge (pH_{pzc}) parameter of GO@MFe_{2}O_{4} nanomaterials can be described for the electrical charge density on a surface coverage, which is ascribed to a zero value [21]. Figure 4 shows the pH_{pzc} values of a range of materials, as follows: MnFe_{2}O_{4}/GO (pH_{pzc} = 6.5) < NiFe_{2}O_{4}/GO (pH_{pzc} = 7.0) < CoFe_{2}O_{4}/GO (pH_{pzc} = 7.3).

In adsorption, note that when pH of solution is lower than pH_{pzc}, the nanocomposite surface is positively charged, leading to an electrostatic force between anions and positive-charged functional groups on surface. By contrast, when pH of solution is greater than pH_{pzc}, the surface is negatively charged and it tends to attract cations from the solution. Especially, when pH of solution is as equal as pH_{pzc}, the electrical density on a surface coverage reaches a zero value, making a balanced status in charge.

3.5. Surface area of GO@MFe_{2}O_{4} (M= Co, Mn, Ni)

Table 1 shows the comparative surface area of GO@MFe_{2}O_{4} nanomaterials, which their values ordered as follows: GO@MnFe_{2}O_{4} (246.39 m^{2}/g) > GO@CoFe_{2}O_{4} (239.57 m^{2}/g) > GO@NiFe_{2}O_{4} (181.12 m^{2}/g). Interestingly, compared with MFe_{2}O_{4} material synthesized via various methods according to several previous reports, herein, these results disclose much higher surface area values [11, 12]. This phenomenon can be explained due to the effect of graphene oxide coated on the structure, providing more new pores such as micro/meso/macropores and thus increasing hierarchically porous structures and high surface areas.

Table 1. BET surface area of GO@MFe_{2}O_{4} (M=Co, Mn, Ni).

| No. | Nanomaterials   | S_{BET} (m^{2}/g) |
|-----|----------------|-------------------|
| 1   | GO@CoFe_{2}O_{4} | 239.57            |
| 2   | GO@MnFe_{2}O_{4} | 246.39            |
| 3   | GO@NiFe_{2}O_{4} | 181.12            |

4. Conclusions

The nanocrystalline graphene oxide-decorated MFe_{2}O_{4} (M = Co, Mn, Ni) MNPs were successfully synthesized from MFe_{2}O_{4} via complex polymerization method and graphene oxide via Hummer’s method. The GO@MFe_{2}O_{4} nanocrystal were structurally characterized using SEM, EDS, FT-IR, and BET techniques. The results indicated that MNPs had the spinel-like agglomeration form, diverse functional groups such as C=O, O-H derived from graphene oxide, and Fe(II)-O and Fe(III)-O bonds at lower frequency bands. Moreover, the values for pH_{pzc} and saturation magnetization obey the following order: MnFe_{2}O_{4}/GO (pH_{pzc} = 6.5 and 1.8 emu/g) < NiFe_{2}O_{4}/GO (pH_{pzc} = 7.0 and 2.4 emu/g) < CoFe_{2}O_{4}/GO (pH_{pzc} = 7.3 and 4.5 emu/g). Especially, the BET surface area were measured to be GO@MnFe_{2}O_{4} (246.39 m^{2}/g) > GO@CoFe_{2}O_{4} (239.57 m^{2}/g) > GO@NiFe_{2}O_{4} (181.12 m^{2}/g), which were much higher than precious reports by other synthesis pathways. These recorded characteristics demonstrated a wide range of promising application trends of GO@MnFe_{2}O_{4} nanocomposites (e.g. adsorption).

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References

[1] L M Rossi, N J S Costa, F P Silva, R Wojcieszak 2014 Green Chem. 16 2906–2933
[2] D Rodriguez-Padron, A R Puente-Santiago, A Caballero, A Benitez, A M Balu, A A Romero, R Luque 2017 J. Mater. Chem. A. 5 16404–16411
[3] M Runowski, S Lis 2016 J. Lumin. 170 484–490
[4] M Nooris, D Aparna, S Radha 2016 Eur. Biophys. J. 45 139–148
[5] Z J Jiang, S Cheng, H Rong, Z Jiang, J Huang 2017 J. Mater. Chem. A. 5 23641–23650
[6] P Dolcet, S Diodati, F Zorzi, P Voepel, C Seitz, S Mascotto, F Nestola, S Gross 2018 Green Chem. DOI: 10.1039/C8GC00086G
[7] Y Ren, L Lin, J Ma, J Yang, J Feng, Z Fan 2015 Appl. Catal. B Environ. 165 572–578
[8] M L Aparna, A N Grace, P Sathyanarayanan, N K Sahu 2018 J. Alloys Compd. 745 385–395
[9] H Zhu, R Jiang, J Li, Y Fu, S Jiang, J Yao 2017 Sep. Purif. Technol. 179 184–193
[10] W Wang, Z Ding, X Zhao, S Wu, F Li, M Yue, J P Liu 2015 J. Appl. Phys. 117 17A328
[11] M Li, Y Xiong, X Liu, X Bo, Y Zhang, C Han, L Guo 2015 Nanoscale. 7 8920–8930
[12] S Sabale, V Jadhav, V Khot, X Zhu, M Xin, H Chen 2015 J. Mater. Sci. Mater. Med. 26 127
[13] L G Bach, D V N Vo, N D Trinh, V T T Ho, T V Tran 2018 Applied Mechanics and Materials 876 46–51
[14] X Zhu, H Zhao, X Niu, T Liu, L Shi, M Lan 2016 Microchim. Acta. 183 2431–2439.
[15] Y Li, J Shen, Y Hu, S Qu, G Min, Z Song, Z Sun, C Li 2015 Ind. Eng. Chem. Res. 54 9750–9757
[16] H Xia, D Zhu, Y Fu, X Wang 2012 Electrochim. Acta. 83 166–174
[17] P N Medeiros, Y F Gomes, M R D Bomio, I M G Santos, M R S Silva, C A Paskocimas, M S Li, F V Motta 2015 J. Adv. Ceram. 4 135–141
[18] S Suresh, A Prakash, D Bahadur 2018 J. Magn. Magn. Mater. 448 43–51
[19] M H Beyki, F Shemirani, J Malakootikhah, S Minaeian, R Khani 2018 React. Funct. Polym. 125 108–117
[20] Z Naghshbandi, N Arsalani, M S Zakerhamidi, K E Geckeler 2018 Appl. Surf. Sci. 443 484–491
[21] L G Bach, T Van Tran, T D Nguyen, T Van Pham, S T Do 2018 Res. Chem. Intermed. 44 1661–1687
[22] T Van Thuan, B T P Quynh, T D Nguyen, V T T Ho, L G Bach 2017 Surfaces and Interfaces 6 209–217
[23] T Van Tran, Q T P Bui, T D Nguyen, V T T Ho, L G Bach 2017 Water Sci Technol. 75 (9-10) 2047–2055
[24] V T Tran, V T Pham, T P Q Bui, D T Nguyen, L G Bach 2017 Vietnam Journal of Science, Technology and Engineering 59 3–6
[25] T V Tran, Q T P Bui, T D Nguyen, N T H Le, L G Bach 2017 Adsorpt. Sci. Technol. 35 72–85
[26] T Tran, T D Nguyen, V T T Ho, Q T P Bui, L G Bach 2017 Journal of Materials and Environmental Science 8 (2) 426–437
[27] D Wang, G Zhang, L Zhou, M Wang, D Cai, Z Wu 2017 Langmuir 33 7007–7014
[28] J Xu, Z Li, X Yue, F Xie, S Xiong 2018 Anal. Methods. 10 2026-2033
[29] Z Li, Y Xiang, S Lu, B Dong, S Ding, G Gao 2018 J. Alloys Compd. 73 58–66
[30] N I Zaaba, K L Foo, U Hashim, S J Tan, W-W Liu, C H Voon 2017 Procedia Eng. 184 469–477
[31] L Yan, Y Yin, P Lv, Z Zhang, J Wang, F Long 2016 J. Agric. Food Chem. 64 3091–3100
[32] Q Zhao, H Zhao, L Yan, M Bi, Y Li, Y Zhou, Z Song, T Jiang 2017 J. Nanosci. Nanotechnol. 17 28–31.
[33] C Si, Y Zhang, C Zhang, H Gao, W Ma, L Lv, C Zhang 2017 Electrochim. Acta. 245 829–838
[34] C Wei, Z Feng, M Baisarayev, L Yu, L Zeng, T Wu, H Zhao, Y Huang, MJ Bedzyk, T Sritharan, ZJ Xu 2016 Chem. Mater. 28 4129–4133.
[35] I Ibrahim, I O Ali, T M Salama, A A Bahgat, M M Mohamed 2016 Appl. Catal. B Environ. 181 389–402
[36] Z Xu, C Shen, Y Hou, H Gao, S Sun 2009 Chem. Mater. 21 1778–1780
[37] T V Tran, H T N Le, H Q Ha, X N T Duong, L T H Nguyen, T L H Doan, T Truong 2017 Catalysis Science & Technology 7 3453-3458