



Preparation and Characterization of Magnetic NiFe₂O₄ Decorated Exfoliated Graphite *via* Sol-Gel Method

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Received: 26 September 2019;

Accepted: 28 May 2020;

Published online: 20 August 2020;

AJC-20018

In present study, a composite material was synthesized from expanded graphite (EG) and nickel ferrite (NiFe₂O₄) *via* the sol-gel method. The composite was then structurally and morphologically characterized which confirmed that NiFe₂O₄ is successfully incorporated in the expanded graphite matrix after impregnation. For component characterization, energy diffraction scattering was used. X-ray diffraction (XRD) was employed to determine the physical structure of the nanocomposites. Lastly, pore size structure of EG@NiFe₂O₄ was examined *via* the nitrogen adsorption/desorption isotherm and pore size distribution plot.

Keywords: Expanded graphite, Nickel ferrite, sol-gel method.

INTRODUCTION

In previous years, researchers have focused on the synthesis of clever surface materials with new features applied in biological functional materials, medication transfer systems, bio-chemistry, bioelectronics, regenerative medicine, hybrid materials and surfaces [1-5]. Various advantages of exfoliated graphite (EG) have been discovered including large surface area, excellent thermal stability, non-toxicity, resistance against corrosion and oxidation and excellent heat conductivity [6-8]. The material is conventionally synthesized by various methods including heating rapidly expandable graphite to about 800-1000 °C, ultrasound irradiation or microwave irradiation [9-11]. One notable feature of the production of exfoliated graphite that it an excellent candidate as support catalyst is scalability, which allows production of the material in large quantities at a reasonable cost. Application of exfoliated graphite is diverse including manufacture of gaskets, electrochemicals, sensors and thermal insulators [12]. In addition, it has been recently found that exfoliated graphite could be utilized as a sorbent material [13,14].

Nickel ferrite (NiFe₂O₄), an inverse spinel whose ferric ions are equally distributed in the tetrahedral sites (A-sites) and the octahedral sites (B sites) exhibited various valuable properties including good catalytic activity, stable crystalline structure, low solubility and good ferromagnetic properties [12,15,16]. Such advantages suggest the use of NiFe₂O₄ in manufacture of high density magnetic recording media, magnetic refrigeration, magnetic liquids, or microwave absorber. Despite that one main drawback of NiFe₂O₄ particle synthesis process is the particle aggregation, often due to its high particle surface energy [17]. The phenomenon often causes greatly degraded catalytic activity. This calls for a technique to disperse agglomerate particles.

The current study aims to support NiFe₂O₄ particles on exfoliated graphite *via* a facile sol-gel method. Then, EG@NiFe₂O₄ composites were characterized using several analytical techniques such as XRD, SEM, EDS and N₂ adsorption/desorption isotherm measurements.

EXPERIMENTAL

The chemicals were of commercially purchased from Merck, USA without any purification methods prior to the utili-

zation. Natural graphite samples were purchased from Yen Bai province, Vietnam.

Synthesis of magnetic NiFe₂O₄ decorated exfoliated graphite by sol-gel method: Typically, the process commenced with the addition of 1 mmol of NiCl₂·6H₂O and 2 mmol of FeCl₃·6H₂O into 60 mL of water. The mixture was stirred to 90 °C then, added citric acid solution in a molar ratio of 4:1 (citric acid:Fe³⁺) and allowed the mixture reacted at 90 °C for 1 h. Expanded graphite (EG) was added in a reaction mixture in molar ratio of 3:1 (EG/MFe₂O₄) slowly and slightly stirred, pH solution about 7-8. After that pH was again adjusted until the plank appears on the surface of the reaction vessel. Gel was dried at 80 °C for 20 h and finally, the muffle kiln was used to peel off the graphite layers.

Instruments: X-ray powder diffraction (XRD) profiles were recorded via the D8 Advance Bruker powder diffractometer with the excitation source of CuK α beams. Scanning electron microscope S4800 instrument (Japan) was used to record the sample images at the magnification of 7000 and an accelerated voltage source (15 kV).

RESULTS AND DISCUSSION

FT-IR studies: Fig. 1 depicts the FT-IR spectrum of EG@NiFe₂O₄ composites in the wavelength ranging from 4000-400 cm⁻¹. Two intense bands observed between 454 and 597 cm⁻¹ indicated the stretching vibration modes related to the metal-oxygen absorption bands Fe-O bonds in the crystalline lattice of NiFe₂O₄. These are typical bands for ferrites, which possess the spinel structure. In addition, it was revealed that EG@NiFe₂O₄ exhibited absorbance bands, which were corresponded to the stretching of O-H (3400 cm⁻¹), carbonyl C=C (1639 cm⁻¹), C-O-C and C-O (1191 cm⁻¹), respectively. Lastly, the absorption band at 1014 cm⁻¹ could be indicative of graphite intercalation compound, manifesting as the C-O stretching mode.

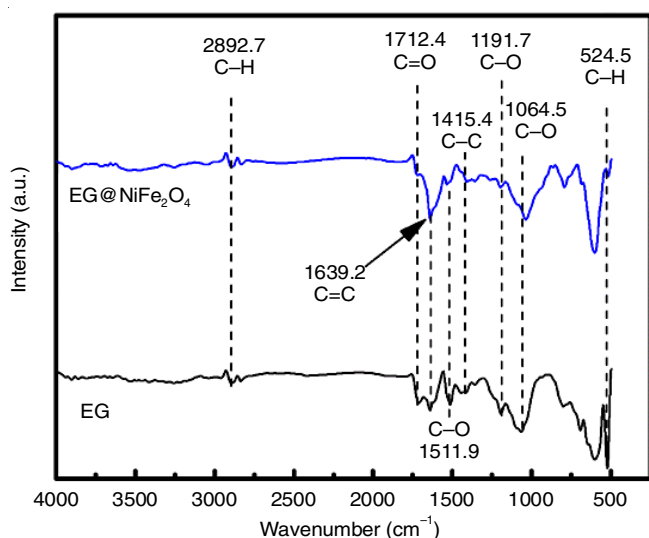


Fig. 1. FT-IR spectrum of EG@NiFe₂O₄.

XRD analysis: The XRD analysis was conducted to compare the crystallinity of EG@NiFe₂O₄ with their precursors including EG and NiFe₂O₄. To determine the phase of material,

X-ray diffraction (XRD) on ARL with X-ray diffraction meter (Cu radiation, $\lambda = 1.5406$ and 1.5443 Å) within the $2\theta = 5^\circ$ range at one continuous scanning speed of 4° per minute was used. From Fig. 2, it is shown that the maximum peak at 26.6° is similar to previous literature [18], indicating the successful synthesis of EG. In the top spectrum of EG@NiFe₂O₄, a sharp peak at 26.6° was again observed as in the bottom spectrum of EG. This confirmed that EG is successfully doped in NiFe₂O₄. The main peaks of EG@NiFe₂O₄ were found at 30.11° , 35.57° , 45.91° , 54.31° , 57.11° , 62.61° , 70.90° and 74.32° . Besides, some peak traces of NiFe₂O₄ may be observed in the spectrum of EG@NiFe₂O₄. However, due to the encapsulation of the peripheral shell of NiFe₂O₄ nanoparticles by EG, the signal of these peak traces was rather weak. This phenomenon may be due to the decoration of non-magnetic EG, leading to a depletion in magnetization and crystallinity of origin NiFe₂O₄.

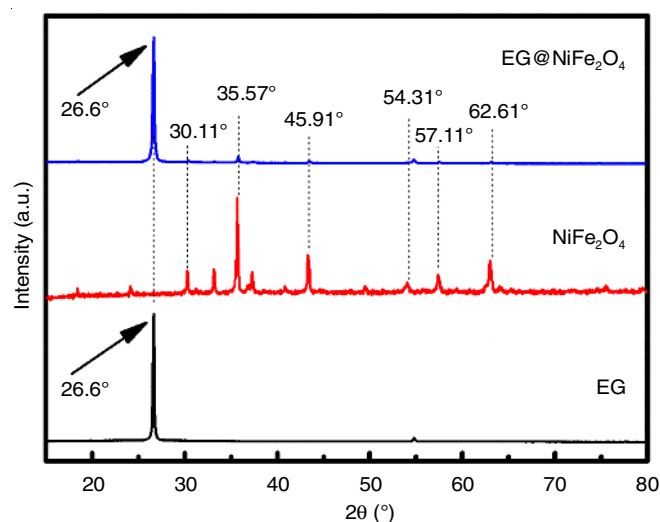


Fig. 2. XRD spectra of EG, NiFe₂O₄ and EG@NiFe₂O₄.

The EG@NiFe₂O₄ nanoparticles were also characterized by SEM. Visually, large grains could be observed in the range of 50-100 nm (Fig. 3). Exfoliating seemed to cause porous solid bodies to form through gas evaporation and sintering of the well-faceted grains during the preparation.

EDS analysis of EG@NiFe₂O₄: Fig. 4 presents energy dispersive X-ray analysis (EDS) results showing regional compositional purity of EG@NiFe₂O₄. The first peak correspond to C of graphite at 0.25 keV. The next second peaks correspond to O at 0.5 keV, Fe K at 0.604 keV and Ni K at 0.612 keV. Moreover, the final peaks correspond Fe K at 6.404 keV and Ni K at 7.5 keV and the third peak corresponds to Ni Kb at 8.3 keV.

BET analysis: The structure of EG@NiFe₂O₄ pore by the nitrogen adsorption/desorption isotherm is displayed in Fig. 5a. Clearly, EG@NiFe₂O₄ material showed an isotherm plot that is commensurate with the typical type IV isotherm. This suggests the presence of mesopore (2-60 nm) of the structure of EG@NiFe₂O₄. Fig. 5b also presents the pore diameter of EG@NiFe₂O₄ from 2 nm to 60 nm. From the BET theory, the BET specific surface area and the pore volume of EG@NiFe₂O₄ were at 22.76 m²/g and 0.136813 cm³/g, respectively, and thus proved to be a suitable and effective adsorbent.

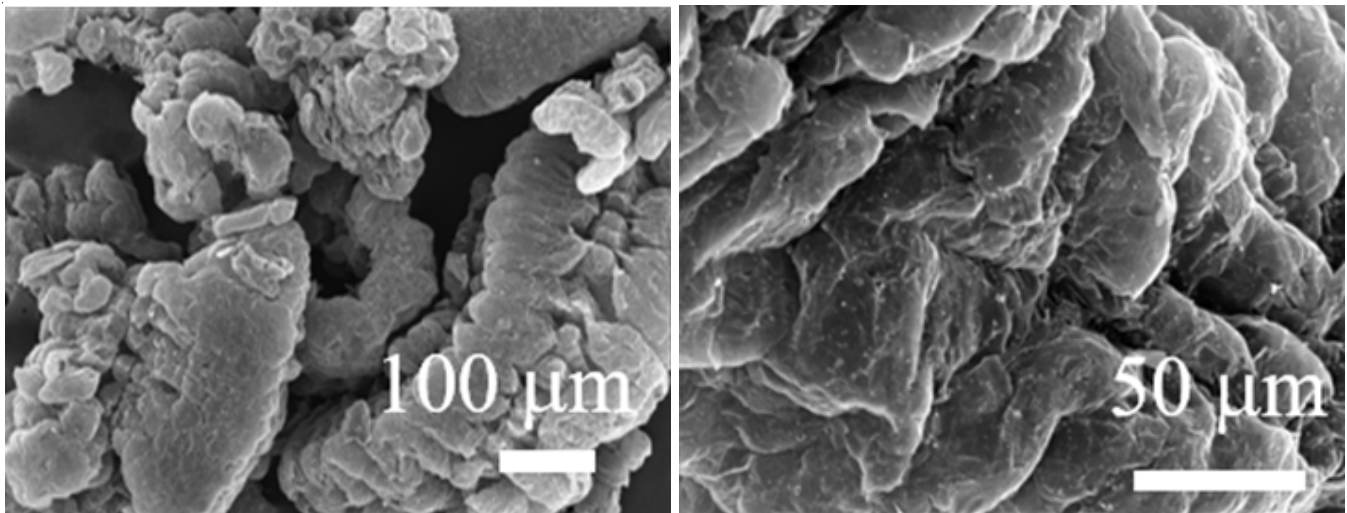


Fig. 3. SEM image of EG@NiFe₂O₄

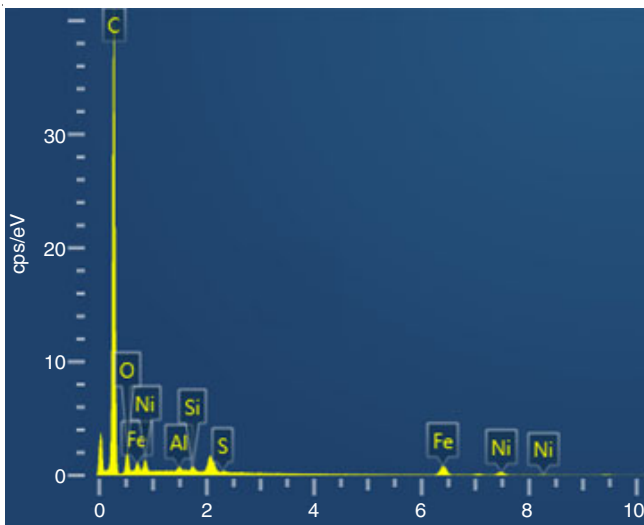


Fig. 4. EDS spectrum of EG@NiFe₂O₄

Conclusion

Natural graphite, an accessible, inexpensive and environmentally friendly material is utilized into fabrication of exfoliated graphite (EG) having several surface functional groups. A nanocomposite of the type EG@NiFe₂O₄ has been prepared by a facile sol-gel technique. The obtained nanocomposite was morphologically, structurally, optically and magnetically characterized by appropriate methods. Chemical bonds of EG@MnFe₂O₄ was investigated using several techniques such as X-ray powder diffraction (XRD), scanning electron microscope (SEM), energy-dispersive X-ray spectroscopy (EDS), nitrogen adsorption/desorption isotherm and pore size distribution.

ACKNOWLEDGEMENTS

This study was supported by grants from Nguyen Tat Thanh University, Ho Chi Minh City, Vietnam.

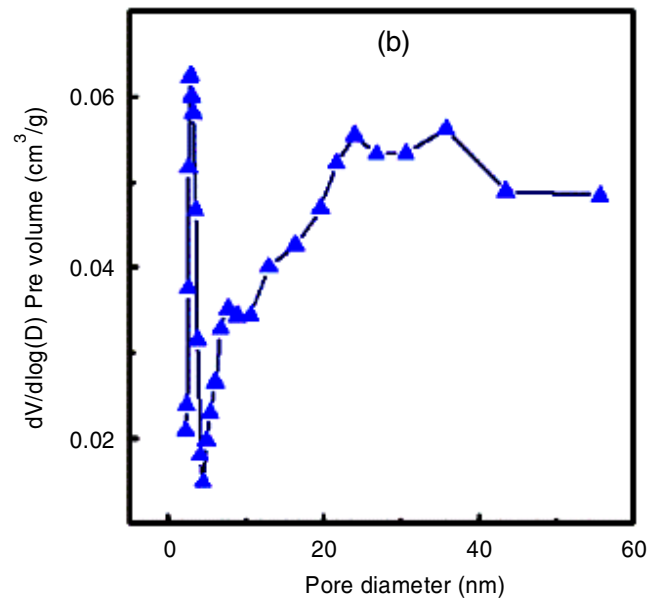
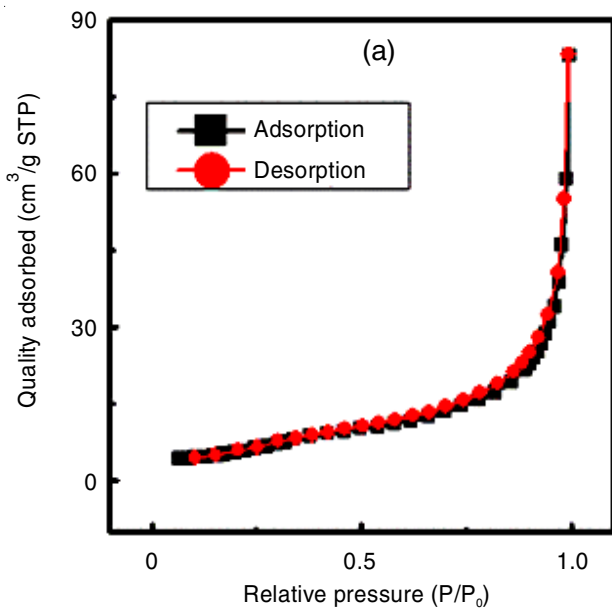


Fig. 5. N₂ adsorption/desorption isotherm (a) and pore size distribution (b) of EG@NiFe₂O₄

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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