Synthesis and Characterization of Magnetic Expanded Graphite Material (EG@CoFe$_2$O$_4$) Through Sol-Gel Processing

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Abstract. The development of novel materials is indispensable to industrial development due to their instrumental role in medical and decontamination applications. Expanded graphite (EG) possesses a number of advantages including pore structure, non-toxicity and ease of recoverability, making it suitable materials for a wide array of possibilities in many fields. In this paper, a material composite based on expanded graphite (EG) and cobalt ferrite (CoFe$_2$O$_4$) was successfully prepared by the direct sol-gel process. The obtained EG@CoFe$_2$O$_4$ was then characterized using a number of analysis techniques including scanning electron microscopy (SEM), X-ray diffraction (XRD), energy dispersive X-ray (EDX) and Fourier transform infrared spectroscopy (FT-IR). The results indicated successful impregnation of CoFe$_2$O$_4$ into the EG matrix. The as-synthesized EG@CoFe$_2$O$_4$ is also uniform and possessed good crystallinity. The isotherm of the obtained EG@CoFe2O4 material seems to follow the typical type IV isotherm and the pore size of the materials ranged from 2-55 nm.

1. Introduction

Recent advances in the study of novel materials have offered the possibility of large-scale production of new adsorbents applicable in the environmental technology, marking a step towards their widespread use in real applications [1-10]. Expanded graphite (EG) is a porous material that has recently gained attention in the field of wastewater treatment as a promising adsorbent due to its advantages including non-toxicity and facilitated recoverability in the aqueous media [11-15]. However, the lightness and brittleness of EG makes its recoverability difficult in real applications.

To tackle the issue, one approach that has been extensively studied is to coat metal oxide nanoparticles on appropriate substrates, resulting in nanocomposites with better functionalities [16,17]. Therefore, the research pathway involving application of exfoliated graphite in manufacture of highly...
applicable nanomaterials has emerged as a growing interest recently and various synthesis routines have been devised to manufacture exfoliated graphite-based composites [18-21].

Cobalt ferrite (CoFe$_2$O$_4$), a magnetic material with diverse functionalities, has been recognized as an instrumental component in critical applications due to low magnetic coercivity, high electrical resistivity, low eddy current loss and excellent chemical stability [22-24]. Such advantages enable CoFe$_2$O$_4$ to be used in targeted drug delivery, sensor, ferrofluids or as an efficient catalyst [25-28]. Among spinel ferrites, CoFe$_2$O$_4$ has been recognized as a favorable candidate for adsorption applications due to many advantages including its capability to control saturation magnetization, mechanical hardness and large magneto-crystalline-anisotropy [1]. In this study, we presented a facile and practical citric acid sol-gel synthesis route to prepare EG@CoFe$_2$O$_4$ composites.

Among such synthesis techniques, the sol-gel process has been shown to have a number of advantages. First, sol-gel technique allows for tight control of stoichiometry of precursor solutions and requires relatively low annealing temperatures. In addition, the method also does not require sophisticated instruments and facilitates compositional modifications and distribution of metal oxide nanoparticles on substrates with large surface [28-31].

2. Materials and method

2.1. Experimental

Using microwave irradiation, the porous EG was fabricated from the natural flaky graphite source. First, a mixture containing Co(NO$_3$)$_2$.6H$_2$O and Fe(NO$_3$)$_3$.9H$_2$O at a molecular ratio of 2: 1 entered the reaction system containing H$_2$O and was mixed well with a glass rod. The mixture was then heated slowly under vigorous stirring on the stove until it reaches 90 °C. Then, m$_1$ (g) of Citric acid solution of 0.02 M concentration (number of moles of acid / number of Fe$^{3+}$ of 4: 1) was added at a rate of 1 drop/sec and the mixture was allowed to react at 90 °C for 1 h. The mixture was then adjusted on pH = 7-8 with NH$_4$OH.H$_2$O solution. After 30 minutes, the pH was adjusted for the second time when the plank appeared on the surface of the reaction vessel. Then, m$_2$ (g) exfoliated graphite (EG) was slowly added (EG@CoFe$_2$O$_4$ ratio 3: 1) and the mixture was gently stirred until EG no longer pushes on the surface in 10 minute. Finally, the gel was dried at 80 °C for 2 h.

![Figure 1. Synthesis diagram of EG@CoFe$_2$O$_4$](image)

2.2. Instrumentation

X-ray powder diffraction (XRD) profiles were recorded using the D8 Advance Bruker powder diffractometer with Cu–Kα beams as excitation sources. Scanning electron microscope (SEM) images of the sample at magnification of 7000 was captured using the S4800 instrument (Japan) operating under an accelerating voltage source (15 kV). FT–IR spectra was recorded on the Nicolet 6700 spectrophotometer to elucidate chemical bonds and functional groups of the sample. Nitrogen adsorption-desorption isotherm (BET) were used to determine the specific area and pore distributions of as-prepared samples by BET formalism and BJH method (TriStar 3000 V6.07 A).
3. Results and discussion

SEM images at 50 and 100 μm magnification of the EG@CoFe$_2$O$_4$ composite were shown in Figure 2. At the weight ratio of EG/CoFe$_2$O$_4$ of 3:1, CoFe$_2$O$_4$ seemed to be well dispersed on the EG surface at sufficient loading amount. At the magnification of 100 μm (Fig.2-Left), EG exhibited a worm-like structure and contained many irregular honeycomb micropores in the layers of graphite. In addition, many molecule seeds could be observed on the EG surface, as expected for CoFe$_2$O$_4$ particles (Fig. 2-Right). In addition, the sol-gel method allows for recombination processes, resulting in firm coating of CoFe$_2$O$_4$ on EG surface and good expansion of EG. These results completely suitable for the previous reports [2][3].

![Figure 2. SEM image of EG@CoFe$_2$O$_4$ composites](image)

Further details on composition and EDX spectrum of the as-synthesized EG@CoFe$_2$O$_4$ composites are presented in Figure 3. The first peak in the EDX spectra corresponding to C of graphite was identified at 0.25 keV. The peak at 0.5 keV could be attributable to the O element. Two peaks at 0.604 and 0.612 keV could be respectively attributable to Fe K and Co K. The peak at 6.404, 6.9303 and 7.649 keV could be respectively index to Fe K, Co K and Co K. Figure 2 also indicates that the peak of C emerges as the primary peak while peaks of other elements such as Fe and Co are considerably smaller and arise from the coating. Combining with the SEM image, it is indicated that the synthesis of EG@CoFe$_2$O$_4$ composites was successful and CoFe$_2$O$_4$ particles were matrixed onto the surface of EG.

![Figure 3. EDX spectrum of EG@CoFe$_2$O$_4$ composites](image)

Figure 4a and 4b respectively demonstrated the nitrogen adsorption/desorption isotherm and the distribution pattern of pore diameter of the as-synthesized EG@CoFe$_2$O$_4$ composites. Referencing to IUPAC, the isotherm of the obtained EG@CoFe$_2$O$_4$ material seems to adhere to the typical type IV isotherm, indicating the mesoporous (2-55 nm) of EG@CoFe$_2$O$_4$ structure. Regarding pore size, it was
shown that the pore diameter of EG@CoFe$_2$O$_4$ seemed to range from 2 nm to 55 nm. Further, theoretical calculation of the BET specific surface area and pore volume of the EG@CoFe$_2$O$_4$ material yielded the value of 29.11 m$^2$/g, and 0.130990 cm$^3$/g, respectively.

![Graph showing N$_2$ adsorption/desorption isotherm and pore size distribution of EG@CoFe$_2$O$_4$ composites]

**Figure 4.** N$_2$ adsorption/desorption isotherm (a) and pore size distribution (b) of EG@CoFe$_2$O$_4$ composites

Figure 5 shows the X-ray diffraction (XRD) spectra of three samples including EG, CoFe$_2$O$_4$ and the as-synthesized EG@CoFe$_2$O$_4$ composites. The main peak detected at $2\theta = 26^\circ$ is consistent with the standard diffraction pattern of EG. In the CoFe$_2$O$_4$ spectra, five peaks identified at 30.11$^\circ$, 35.57$^\circ$, 54.31$^\circ$, 57.11$^\circ$, and 62.61$^\circ$ could be respectively indexed to the (2 2 0), (3 1 1), (4 0 0), (5 1 1) and (4 4 0) planes of CoFe$_2$O$_4$, respectively, suggesting the cubic spinel structure of cobalt ferrite. Apart from characteristic peaks of CoFe$_2$O$_4$ and EG, no additional peak was detected in the spectra, indicating the presence of only the two component in the resulting EG@CoFe$_2$O$_4$. The results indicate the mix phase product of EG and CoFe$_2$O$_4$ and are consistent with previously published studies [21,22].

![XRD pattern of EG@CoFe$_2$O$_4$]

**Figure 5.** XRD patterns of EG@CoFe$_2$O$_4$

Figure 6 illustrated the FT-IR spectrum of EG@CoFe$_2$O$_4$ composites in the range 400-4000 cm$^{-1}$. Two intense bands could be first observed in the range between 454 cm$^{-1}$ and 597 cm$^{-1}$, which is due to the stretching vibration modes of Fe–O bonds in the crystalline lattice of CoFe$_2$O$_4$. This is typical to
spinel structures in general and for ferrites in particular. In addition, three characteristic absorbance bands found at 3400, 1639 and 1191 cm\(^{-1}\) could be attributable to the stretching of O-H, carbonyl C=\(\text{C}\) and C-O-C and C-O respectively. Lastly, the absorption band detected at 1014 cm\(^{-1}\) is index to the C=O stretching mode, which is indicative of graphite intercalation compound.

![FT-IR spectrum of EG@CoFe\(_2\)O\(_4\)](image)

**Figure 6.** FT-IR spectrum of EG@CoFe\(_2\)O\(_4\)

4. Conclusions
The present study has presented a synthesis routine for EG@CoFe\(_2\)O\(_4\) composites using the direct sol-gel process. A number of instrumentations including XRD, SEM, TEM, EDX and FTIR was used to determine the composition, structure, morphology and pore size of as-synthesized EG@CoFe\(_2\)O\(_4\). Generally, uniformity and good crystallinity of the EG@CoFe\(_2\)O\(_4\) were confirmed via XRD spectra and the inverse spinel structure of ferrites was confirmed by FT-IR. Scanning electron microscopy (SEM) and BET surface area observations show that cobalt ferrite nanoparticles with sizes of 2–55 nm are well dispersed on graphite sheets.

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References
[1] Mai L N T, Giang L B, Quynh B B, Vu H T N 2020 *Synthetic Metals* **263** 116355.
[2] Hoa T Q, Thu K T N, Nghia T C, Hugo N and Giang L B 2020 *AIP Advances* **10** 035326.
[3] Thuy C N, Quoc M V, Thuy T P, Quoc T V, An Q V, Giang L B and Thai H 2020 *Journal of Polymers and the Environment* **28** 1795–1810.
[4] Hau Q P, Tai T H, Giang L B, Van and T T H 2020 *International Journal of Hydrogen Energy*.
[5] Trang T K T, Joo W H, Dong W K, Yeun T J, Yeong S G, Giang L B, Yong H K and Kwon T L 2019 *Molecular Crystals and Liquid Crystals* **686**:1 55-62.
[6] Thuan V T, Duyen T C N, Hanh T N L, Loc H H, Thanh T N, Dat V D, Trinh D N, and Giang L B 2012 *Comptes Rendus Chimie*.
[7] Luyen T Tran, Hoang V T, Thu D L, Giang L B, and Lam D T 2019 *Advances in Polymer Technology* **8124351** 9.
[8] Sasha S, Richard D P, Xinqui C and Nianqiang W 2006 *J. Mater. Chem* **16** 155-158.
[9] Thinh V P, Trinh D T, Thuong T T, Van T T H, Quynh T P B, Giang L B 2018 *Solid State Phenomena* **279** 230-234.
[10] Thinh V P, Thuong T N, Trinh D N, Thuan T V, Quynh T P B, Viet D N V and Giang L B 2019 *C Journal of Nanoscience and Nanotechnology* **19** 1122-1125.
[11] Vinh H N, Hieu P N, Thin V P, Diep M T N, Thuan N V, Trinh D N, Thuy H N, Giang L B and Quynh P T B 2018 *Journal of Nanoscience and Nanotechnology* **18** 6859-6866.
[12] Bich N H, Thuong T N, Sang T N, Quynh T P B and Giang L B 2019 *Cogent Engineering* **6**: 1584939.
[13] Dong W K, Giang L B, Seong-Soo H, Chan P, and Kwon T L 2014 *Molecular Crystals and Liquid Crystals* **599** 43–50.
[14] Andrei I V, Julia A P, Igor L K, Natalia V M, Pavel B D, and Artem P M 2018 *Materials Today: Proceedings* **5** 26010-26017.
[15] Zheng K, Boccaccini A R 2017 *Advances in Colloid and Interface Science* **249** 363-373.
[16] Liau L C K, Huang J S 2017 *Journal of Alloys and Compounds* **702** 153-160.
[17] Muscas G, Jovanović S, Vukomanović M, Spreitzer M, and Peddis D *Journal of Alloys and Compounds* **796** 203-209.
[18] Kavitha S, Kurian M 2019 *Journal of Alloys and Compounds* **799** 147-159.
[19] Nguyen H D T, Hong T N, Thuong T N, Thi A K L, Trinh D N, Quynh T P B, and Giang L B The Materials 2019 **12** 1913.
[20] Thin V P, Tham H T N, D.T.C. Nguyen, Nhan H T L, Thuong T N, Lim K T, Trinh D N, Thuan V T, and Giang L B 2109 *Processes 2019*, **7**, 305.
[21] Lazarević Z Z, Jovalekić C, Sekulić D, Slankamenac M, Romčević M and Milutinović A 2012 *Sci. Sinter* **44**.
[22] Li Y, Gao B, Wu T, Wang B and Li X 2009 *J. Hazard. Mater* **164** 1098–1104.
[23] Bing Z, Yunhai W, Yang F 2019 *Journal of Inorganic and Organometallic Polymers and Materials* **29** 290–301.
[24] Bharali D, Deka R C 2017 *J. Environ. Chem. Eng* **5** 2056–2067.
[25] Zong M, Huang Y, Ding X, Zhang N, Qu C and Wang Y 2014 *Ceram. Int.* **40** 6821–6828.
[26] Guedidi H, Reinert L, Lévêque J M, Soneda Y, Bellakhal N and Duclaux L 2013 *Carbon N. Y.* **54** 432–443.
[27] Rahmayeni, Zulhadjri, Jamarun N, Emriadi and Arief S 2016 *Orient. J. Chem.* **32** 1411–1419.
[28] Wang Y, Yang P, Liu G, Xu L, Jia M, Zhang W and Jiang D 2008 *Catal. Commun* **9** 2044–2047.
[29] Anantharaj S, Karthick K and Kundu S 2017 *Mater. Today Energy* **6** 1–26.
[30] Naseem K, Farooqi Z H, Begum R and Irfan A 2018 *J. Clean. Prod.* **187** 296–307.
[31] Ensafi A A, Hosseini A A, Jafari A, Rezaei B, Ghazaei F 2016 *Materials science and engineering C* **60** 276-284.