Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2023.29483

291 (2023) 144–147
April

A facile method to synthesize LDH/GO@α- FeOOH composites

Li-ping Wei, Ping Yang, Hui-qiang Li*

College of Architecture and Environment, Sichuan University, Chengdu 610065, China, Tel.: +8618980668020; email: lhq_scu@163.com (H.-q. Li), Tel.: +8613197233099; email: 2941568634@qq.com (L.-p. Wei), Tel.: +8618602804508; email: yping63@163.com (P. Yang)

Received 18 November 2022; Accepted 14 March 2023

ABSTRACT

In the present work, an original method for the preparation of Fe-LDH composites is discussed. The method is based on chemical modification of layered double hydroxides (LDH). The obtained composites are investigated by scanning electron microscopy and energy-dispersive spectroscopy, X-ray photoelectron spectroscopy, and X-ray powder diffraction patterns. The results reveal that the surface of LDH/GO composites are uniformly assembled by needle-like α-FeOOH with length in the range of 150–300 nm. The loading capacity of α-FeOOH is about 564 mg-Fe/g.

Keywords: Layered double hydroxides; Graphene oxides; α-FeOOH

1. Introduction

Fe-based materials have been used in many areas owing to their interesting physical properties, electrochemical catalytic activities, and feasibilities for mass production with low cost [1–3]. Goethite is a common Fe(III) oxide-hydroxide (α-FeOOH) in soils and sediments, which shows excellent performance in catalysis [1], adsorption [4], supercapacitor [5] and many other fields. Wang et al. demonstrated α-FeOOH crystal show catalytic activity superior to Fe_3O_4 and Fe_2O_3 [6]. Granular α-FeOOH has been successfully used as catalyst for decomposition of aqueous ozone solution, which enhances the catalyst loading from 2 to 30 g/L and increases the percentage of ozone decomposition from 53.2% to 98% [7]. Iron-oxide-based nanoparticles have attracted attentions owing to their huge specific surface area resulting from their small sizes [8]. However, their small size and instability restrict their use in real application. In order to overcome these difficulties, the iron oxide nanoparticles have been tried to load on other substrates, such as zeolite, mesoporous silica, polymeric materials and so on. Hybrid materials composed of FeOOH have been suggested as catalysts for oxygen reduction reactions. Lee et al. [1] prepare novel FeOOH/reduced graphene oxide hybrids, which show good electrochemical catalytic activity. However, the preparation of the hybrid materials usually requires high temperature treatment and complicated operation. Hybrids of graphene oxides (GO) and layered double hydroxides (LDHs) are promising materials due to their versatile properties, which are considered as a potential building block for new materials. There have been rare articles on the synthesis and application of Fe-based LDH-GO materials.

Herein, we report a simple, effective and environment-friendly method for preparing LDH/GO@α-FeOOH composites by ultrasonic-assisted in situ hydrolysis of the precursor ferrous iron on LDH-GO sheets. To the best of our knowledge, it is the first time to report the synthesis of ultrathin LDH/GO@α-FeOOH composites via a one-pot facile hydrothermal method without the use of any adscititious surfactants or templates.

2. Material and methods

Purified natural graphite powder is purchased from Sinopharm Chemical Reagent Co., Ltd., (China). Other reagents are analytical grade and purchased from Sigma-Aldrich (Shanghai) Co., Ltd., without further purification.

* Corresponding author.

GO is synthesized by Hummers methods as described elsewhere [9]. The LDH/GO composites are synthesized via co-precipitation method [10]. For fabrication of LDH/GO@α-FeOOH, 0.5 g synthesized LDH/GO is added to 1,000 mg/L $FeCl_2 \cdot 4H_2O$ solutions. The mixed solution is stirred for 24 h at 25°C, and then is sonicated for 1 h. The precipitate is centrifuged, washed with deionized water thoroughly with distilled water until the washings are neutral. The precipitate is then vacuum dried overnight. The resulting powder is designated as LDH/GO@α-FeOOH. The α-FeOOH are uniformly self-assembled on the surface of LDH/GO nanosheets. The loading capacity of α-FeOOH is calculated to be 564 mg-Fe/g.

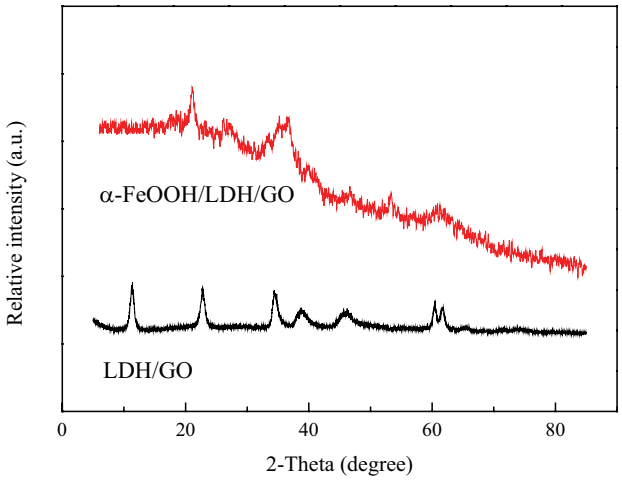

Fig. 1. X-ray powder diffraction patterns of the synthesized composites.

The images of synthesized samples are captured by a scanning electron microscope (SEM) (JSM-7500F, Japan). The X-ray powder diffraction (XRD) patterns are carried out by a powder diffractometer using Cu Kα radiation at a scanning speed of 2°min^{-1} (PANalytical B.V., Holland). The X-ray photoelectron spectroscopy (XPS) tests are measured on an AXIS Ultra DLD (Shimadu, Japan) using monochromatic Al Ka X-ray source.

3. Results

The powder XRD patterns of the synthesized samples are illustrates in Fig. 1. The LDH/GO particles are principally composed of a hexagonal LDHs phase. The LDH/GO exhibits well-developed layer structure with narrow, symmetric, strong peaks at low 2θ values reflection and weaker,

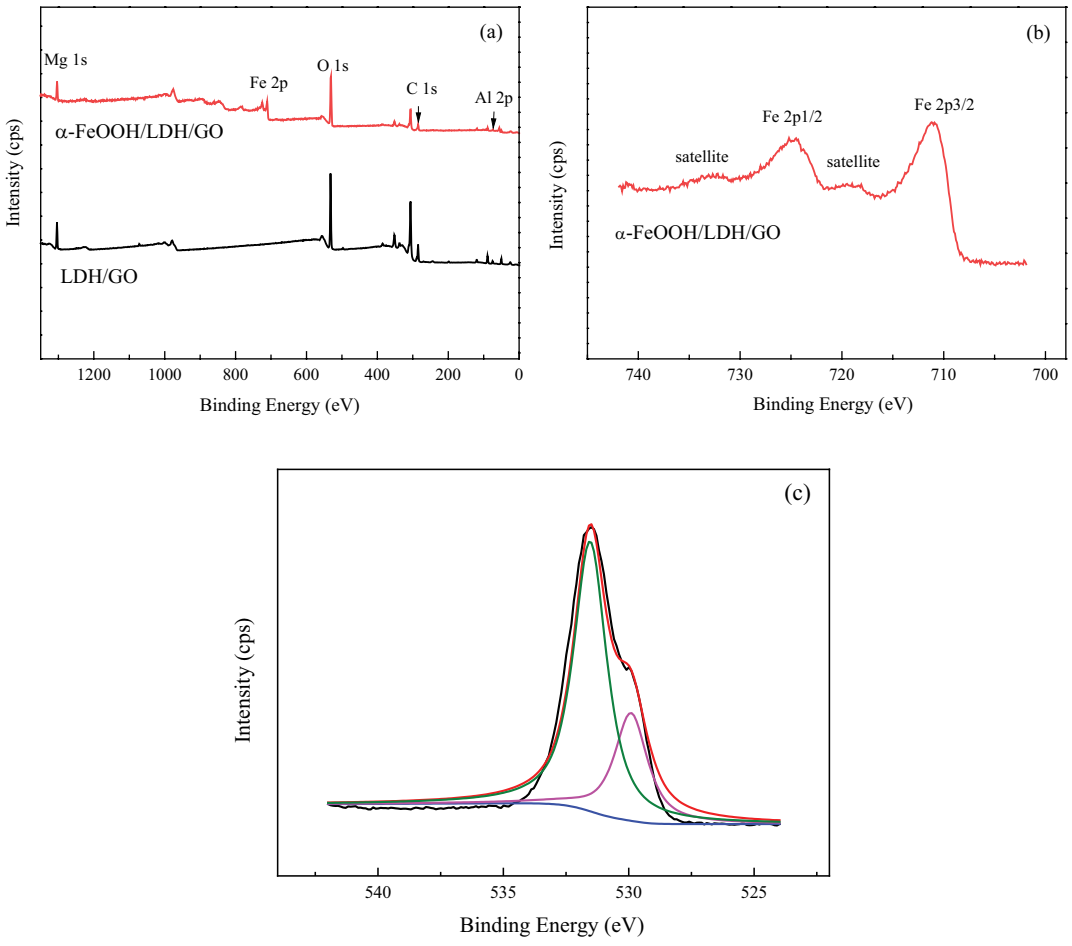

Fig. 2. (a) Wide scan, (b) Fe 2p and (c) O 1s X-ray photoelectron spectroscopy spectra of the synthesized composites.

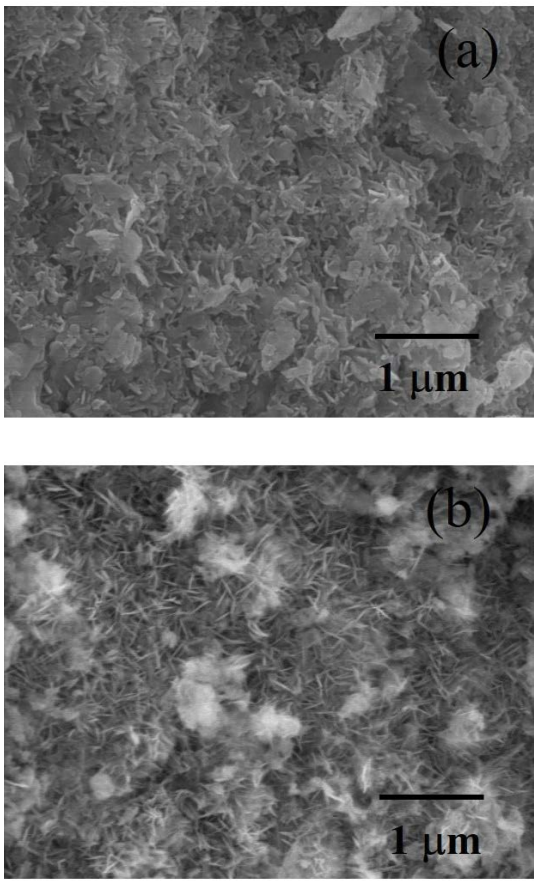

Fig. 3. Scanning electron microscope of (a) LDH/GO and (b) a-FeOOH/LDH/GO.

less symmetric lines at high 2θ values [11]. The main phases of LDH/GO@α-FeOOH are indexed as FeOOH [8,12], and there is no conspicuous peak attributed to the LDH/GO, suggesting the FeOOH totally covered and replaced the LDH/GO phases.

Fig. 2a shows the survey XPS spectra of LDH/GO and LDH/GO@α-FeOOH composites. The most significant features in these spectrums are the Fe 2p, O 1s, and C 1s signals. The peaks due to Fe reveal the presence of Fe species in the obtained composites. The detail spectra of the Fe 2p is illustrated in Fig. 2b. The peaks observed at ~725 and ~711 eV can be assigned to Fe 2p1/2 and Fe 2p3/2, respectively, in good agreement with the binding energy values of Fe^{3+} in FeOOH [8,13]. In addition, the satellite peak of Fe 2p1/2 at ~733 eV and satellite peak of Fe 2p3/2 at ~719 eV are also seen [13]. The O 1s peaks (Fig. 2c) are fitted with Fe–O at 529.9 eV and Fe–OH at 531.5 eV for α-FeOOH.

The morphologies of the obtained samples are investigated by SEM observation. SEM image of the LDH/GO (Fig. 3a) shows that the LDH sheets arrays grow on both sides of the graphene oxides sheets. The inhomogenous flakes are smooth and flat. The GO sheets avoid the flakes stacked together to form agglomerates to some extent [14]. The needle-like FeOOH can be observed on the surface of LDH/GO@α-FeOOH. Fig. 3b presents the morphology of the LDH/GO@α-FeOOH composites, which shows a needle-like morphology with homogeneous size distribution. The lengths of the needles are in the range of 150–300 nm.

4. Conclusions

In summary, we have developed a simple one-pot, green method for the synthesis of the LDH/GO@α-FeOOH composites. What is worth to mention is that the loading capacity of α-FeOOH on LDH/GO is large, which is about 564 mg-Fe/g. It is found that the needle-like α-FeOOH with lengths in the range of 150–300 nm are fully and homogenously coat with LDH/GO composites. The results of XRD and XPS confirm the deposition of α-FeOOH on the surface of LDH/GO. The results of XPS show the existence of the Fe^{3+} valence state, and the estimated amount of iron in the composite is 12.74% (atomic%). The superiority of this system lies in the fact that the combination of the properties of two functional materials can be used to achieve a wide range of application.

Acknowledgments

This research was supported by the International Scientific and Technological Innovation and Cooperation Project of Sichuan (No. 2019YFH0170).

References

[1] S. Lee, J.Y. Cheon, W.J. Lee, S.O. Kim, S.H. Joo, S. Park, Production of novel FeOOH/reduced graphene oxide hybrids and their performance as oxygen reduction reaction catalysts, Carbon, 80 (2014) 127–134.
[2] Y. Sun, X. Hu, W. Luo, H. Xu, C. Hu, Y. Huang, Synthesis of amorphous FeOOH/reduced graphene oxide composite by infrared irradiation and its superior lithium storage performance, ACS Appl. Mater. Interfaces, 5 (2013) 10145–10150.
[3] L. Yu, J. Chen, Z. Liang, W. Xu, L. Chen, D. Ye, Degradation of phenol using Fe_3O_4-GO nanocomposite as a heterogeneous photo-Fenton catalyst, Sep. Purif. Technol., 171 (2016) 80–87.
[4] D.-W. Cho, C.-M. Chon, H. Yang, Y.F. Tsang, H. Song, Effect of Mn substitution on the oxidation/adsorption abilities of iron(III) oxyhydroxides, Clean Technol. Environ. Policy, 20 (2018) 2201–2208.
[5] Y. Wei, R. Ding, C. Zhang, B. Lv, Y. Wang, C. Chen, X. Wang, J. Xu, Y. Yang, Y. Li, Facile synthesis of self-assembled ultrathin alphα-FeOOH nanorod/graphene oxide composites for supercapacitors, J. Colloid Interface Sci., 504 (2017) 593–602.
[6] Y. Wang, M. Liang, J. Fang, J. Fu, X. Chen, Visible-light photo-Fenton oxidation of phenol with rGO-alphα-FeOOH supported on Al-doped mesoporous silica (MCM-41) at neutral pH: performance and optimization of the catalyst, Chemosphere, 182 (2017) 468–476.
[7] M. Muruganandham, J.J. Wu, Granular α-FeOOH – a stable and efficient catalyst for the decomposition of dissolved ozone in water, Catal. Commun., 8 (2007) 668–672.
[8] F. Peng, T. Luo, L. Qiu, Y. Yuan, An easy method to synthesize graphene oxide–FeOOH composites and their potential application in water purification, Mater. Res. Bull., 48 (2013) 2180–2185.
[9] W.S. Hummers Jr., R.E. Offeman, Preparation of graphitic oxide, J. Am. Chem. Soc., 80 (1958) 1339, doi: 10.1021/ja01539a017.
[10] R. Xie, G. Fan, Q. Ma, L. Yang, F. Li, Facile synthesis and enhanced catalytic performance of graphene-supported Ni nanocatalyst from a layered double hydroxide-based composite precursor, J. Mater. Chem. A, 2 (2014) 7880, doi: 10.1039/c4ta00395k.
[11] X.-R. Wang, Y. Li, L.-P. Tang, W. Gan, W. Zhou, Y.-F. Zhao, D.-S. Bai, Fabrication of Zn-Ti layered double hydroxide by varying

cationic ratio of Ti^{4+} and its application as UV absorbent, Chin. Chem. Lett., 28 (2017) 394–399.
[12] S. Sheshmani, M. Akhundi Nematzadeh, S. Shokrollahzadeh, A. Ashori, Preparation of graphene oxide/chitosan/FeOOH nanocomposite for the removal of Pb(II) from aqueous solution, Int. J. Biol. Macromol., 80 (2015) 475–480.
[13] S. Wu, J. Lu, Z. Ding, N. Li, F. Fu, B. Tang, Cr(VI) removal by mesoporous FeOOH polymorphs: performance and mechanism, RSC Adv., 6 (2016) 82118–82130.
[14] L. Tan, Y. Wang, Q. Liu, J. Wang, X. Jing, L. Liu, J. Liu, D. Song, Enhanced adsorption of uranium(VI) using a three-dimensional layered double hydroxide/graphene hybrid material, Chem. Eng. J., 259 (2015) 752–760.