Materials Science & Engineering B 224 (2017) 125–138

Contents lists available at ScienceDirect

Materials Science & Engineering B

journal homepage: www.elsevier.com/locate/mseb

Zinc ferrite composite material with controllable morphology and its applications

Ming Qin[a], Qin Shuai[a,*], Guanglei Wu[c], Bohan Zheng[d], Zhengdong Wang[e], Hongjing Wu[b,*]

[a] Faculty of Materials Science and Chemistry, China University of Geosciences, Wuhan 430074, PR China
[b] Department of Applied Physics, Northwestern Polytechnical University, Xi'an 710072, PR China
[c] Institute of Materials for Energy and Environment, State Key Laboratory Breeding Base of New Fiber Materials and Modern Textile, College of Materials Science and Engineering, Qingdao University, Qingdao 266071, PR China
[d] School of Materials Science and Engineering, Chang'an University, Xi'an 710064, PR China
[e] Center of Nanomaterials for Renewable Energy (CNRE), State Key Laboratory of Electrical Insulation and Power Equipment, School of Electrical Engineering, Xi'an Jiaotong University, Xi'an 710049, PR China

ARTICLE INFO

Keywords:
Zinc ferrite
Chemical synthesis
Modification
Application

ABSTRACT

$ZnFe_2O_4$ is an attractive material due to its unique properties and various applications. A large volume of works on the synthesis of $ZnFe_2O_4$ have been reported such as mechanochemical synthesis, co-precipitation method, sol-gel auto-combustion method, electrospinning method, hydrothermal/solvothermal method, and spray drying. The synthetic methodologies have significant influence on the properties, morphologies and structures of the $ZnFe_2O_4$. Moreover, with the Fe^{3+} and Zn^{2+} substituted by different metal ions, the properties of $ZnFe_2O_4$ can be altered. Besides, the zinc ferrite composites with controlled morphologies and structures have been investigated. Owing to the enhanced magnetic, electrical and catalytic properties of the zinc ferrite composites, extensive applications of zinc ferrite composites have been achieved. In this review, we summarized the synthetic methods as well as the modifications of the $ZnFe_2O_4$. The review also dealt with applications of the $ZnFe_2O_4$ and its composites in the fields of sensors, photocatalysis and lithium ion batteries, etc.

1. Introduction

In recent years, zinc ferrite has been widely investigated due to its unique magnetic [1], electrical properties [2], microwave absorption [3] and photocatalytic properties [4]. However, with the improvement of synthetic method and the combination of novel functional materials, zinc ferrite with controllable morphology and structure or the zinc ferrite composite can be produced which dramatically improve the application of the zinc ferrite materials.

Zinc ferrite is a traditional spinel ferrite and the structure is shown in Fig. 1. Zn^{2+} ions occupy in the tetrahedral A-sites whereas the Fe^{3+} ions occupy in the octahedral B-sites, thus the zinc ferrite is a normal spinel structure. In the normal spinel structure, the magnetic moment is arranged in the opposite direction and the size is equal, so that the magnetic moment of the ferrite is counteracted and the magnetism is not displayed. When the Zn^{2+} ions partially occupy in octahedral B-sites caused by the changing of the temperature the intermediate spinel ferrite is obtained and exhibits ferrimagnetism.

The variation in properties of $ZnFe_2O_4$ is not only influenced by size effect but also due to the incorporating of the foreign ions and novel functional materials. When modifying the zinc ferrite with the introduction of metallic ions, the ion dimension, site preference of the substituent ion, extent of substitution and synthetic method, etc. have a significant influence on the distribution of Zn^{2+}, Fe^{3+} and the foreign cation over the tetrahedral and octahedral sites, which results in the variation of the magnetic and electrical properties. Moreover, large volume of works on the $ZnFe_2O_4$ composites has been reported due to the enhanced performance on the different applications. Considering both of the types of the composite materials and the morphology and structure affect the properties of zinc ferrite composites, the $ZnFe_2O_4$ composites are briefly concluded based on the types of the composite materials in this review. The major purpose of this review is to summarize the synthesis, modification and applications of $ZnFe_2O_4$ in recent years.

2. Synthetic methods and their influence on properties of zinc ferrite

The properties of the materials mainly depend on the different synthetic methods, so it is necessary for us to discuss the ways to

* Corresponding authors.
E-mail addresses: shuaiqin@cug.edu.cn (Q. Shuai), wuhongjing@mail.nwpu.edu.cn (H. Wu).

http://dx.doi.org/10.1016/j.mseb.2017.07.016
Received 14 May 2017; Received in revised form 14 July 2017; Accepted 26 July 2017

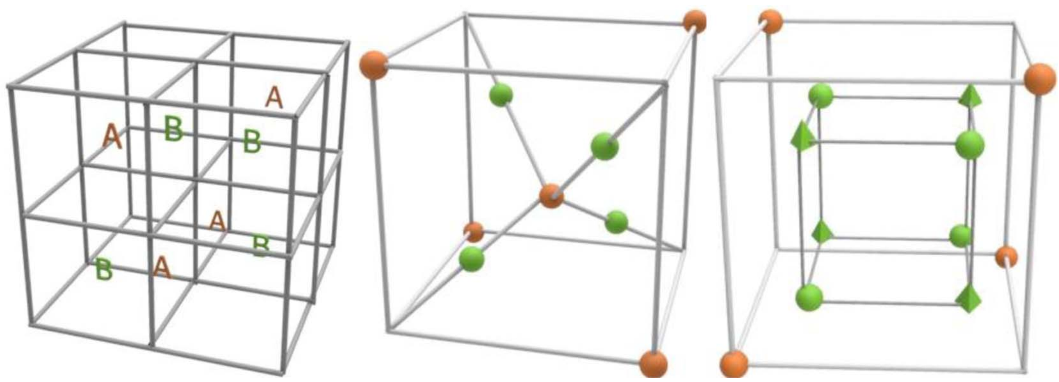

Fig. 1. The crystal structure of zinc ferrite in which the ● represent the Zn^{2+}, the ● represent the Fe^{3+} and the ▲ represent the O^{2-}.

Table 1
The synthetic methods for different morphologies of $ZnFe_2O_4$ and its composites and their application fields.

Materials	Precursors	Synthetic method	Morphologies	Application	Ref.
$ZnFe_2O_4$	$Zn(CH_3COO)_2{\cdot}2H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, PVP	Electrospinning	Nanofibers/nanorods	Anode materials for LIBs	[14]
$ZnFe_2O_4$	$FeCl_3{\cdot}6H_2O$, $ZnCl_2$, NH_4Ac, EG	Solvothermal	Hollow nanospheres/ nanosheets	Microwave absorber	[32]
$ZnFe_2O_4$	*n*-pentanol, $Zn(NO_3)_2$, $H_2C_2O_4$, TAB, cyclohexane, $FeSO_4$	Microemulsion	Nanorods	Ethanol sensor	[33]
$ZnFe_2O_4$	$Zn(NO_3)_2{\cdot}6H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, dextrin	Spray drying	Yolk-shell	Anode materials for LIBs	[35]
$ZnFe_2O_4$	$ZnSO_4{\cdot}7H_2O$, $FeSO_4{\cdot}7H_2O$, EG, oxalic acid	Spray drying	Porous nanorods	Anode materials for LIBs	[36]
$Co_3O_4/ZnFe_2O_4$	$Zn(NO_3)_2{\cdot}6H_2O$, $Fe(acac)_3$, DMF, H_2BDC, Co_3O_4 nanocages	Solvothermal	Hollow Starfish-Shaped	Electrode material for supercapacitor	[51]
$ZnO/ZnFe_2O_4$	$Zn(CH_3COO)_2{\cdot}2H_2O$, $FeSO_4$, $Na_3C_6H_5O_7{\cdot}2H_2O$, ammonia	A mild two-step method	Inner hollow microspheres surrounded by outer nanosheets	Gas sensors	[52]
$ZnFe_2O_4$@C	Cyclohexane, EG, CTAB, oxalic acid,$ZnSO_4{\cdot}7H_2O$, $FeSO_4{\cdot}7H_2O$	In situ graft copolymerization	3-Dimensional cuboid nano-whiskers	Anode materials for LIBs	[55]
CMSs@$ZnFe_{24}$/ Ag_3PO_4	$Zn(NO_3)_2{\cdot}6H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, $CH_3COONa{\cdot}3H_2O$, glucose, EG, $AgNO_3$, $Na_2HPO_4{\cdot}12H_2O$, ethanol	Solvothermal and in situ precipitation	Core-shell	Photocatalyst for 2,4-DCP degradation	[62]
$ZnO/ZnFe_2O_4$@ carbon	$Zn(NO_3)_2{\cdot}6H_2O$, $Fe(acac)_3$, PVP, H_2BDC, DMF	One-step carbonization of Zn/Fe MOFs	Hierarchical ball-in-ball nanospheres	Anode materials for LIBs	[63]
$ZnFe_2O_4$	$Zn(NO_3)_2{\cdot}6H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, urea, glycerol, isopropanol	Solvothermal	Hierarchical yolk-shell microspheres	Acetone sensors	[67]
$ZnFe_2O_4$	$Zn(NO_3)_2{\cdot}6H_2O$, $Fe(NO_3)_3{\cdot}9H_2O/(NH_4)_2Fe(SO_4)_2$, $ZnSO_4$, $H_2C_2O_4/FeCl_2{\cdot}4H_2O$, $ZnCl_2$, urea, $C_6H_8O_6$/Zn $(NO_3)_2{\cdot}6H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, glucose	Hydrothermal	Nanoparticles/nanorods/nano-flowers/hollow microspheres	Photo-Fenton degradation of dyes	[71]

synthesize $ZnFe_2O_4$. $ZnFe_2O_4$ can be synthesized by various synthetic methods such as mechanochemical synthesis, co-precipitation method, sol-gel auto-combustion method, electrospinning method, hydrothermal/solvothermal method, and spray drying. And the methods for the fabrication of $ZnFe_2O_4$ will be briefly introduced in Table 1.

2.1. Sol-gel auto-combustion method

Sol-gel auto-combustion method was briefly concluded as the following steps: metal nitrate and fuel mixed in solution to form metal complexes; solution containing the metal complexes forming xerogel by sol-gel process; the combustion of xerogel in the air. Compared to the traditional sol-gel method, the method is a combination of the sol-gel method and self-propagating synthesis, which makes it own advantages such as controlling the purity and particle size of the target product due to the heat released by the oxidation of organic complexing agents. The types of complexing agent, pH, annealing time, and temperature will affect the yield of the final product.

Mahmoudzadeh et al. [5] investigated the different kinds of fuel additives at different molar ratios to the influence of the zinc ferrite. Glycine, urea and thiourea were chosen as the fuel additives at three different molar ratios to metal nitrates of 1.2:1, 2:1, and 3:1. The result demonstrated that the fuel additives and its molar ratios to metal nitrates affected not only the microstructure but also the crystallite size of the $ZnFe_2O_4$. The pure $ZnFe_2O_4$ was obtained at the condition of thiourea fuel additive at 1:1.2 and 1:2 molar ratios.

Yadav et al. [6] prepared the $ZnFe_2O_4$ nanoparticles by sol-gel auto-combustion method with the starch as the fuel. A further annealing process at temperature of 400, 600, and 800 °C was displayed to obtain the $ZnFe_2O_4$ nanoparticles. The result depicted the crystallite size and lattice parameter increased with a higher annealing temperature. The variation of the annealing temperature also resulted in the change of dielectric and electrical properties.

Sutka et al. [7] synthesized $ZnFe_2O_4$ at three different combustion conditions, (i) xerogel in chamotte crucible and muffle oven; (ii) xerogel in chamotte crucible and open air; (iii) xerogel in the form of a thick layer (1 mm) in open air. The pure $ZnFe_2O_4$ was obtained only under the third condition due to the appropriate oxygen content inside the reaction environment.

Despite the advantages discussed above, there still some drawbacks exist such as the xerogel fabricated by the heating of the solution is easy to crack and the agglomeration of the zinc ferrite powders during the synthetic process.

2.2. Co-precipitation method

Co-precipitation method is a widely used wet chemical synthesis method. The mixed of each component can be carried out at the molecular or atomic level that means we can control the doping content precisely. The nanopowders produced by the method have several