Preparation and characterization of magnetic $\alpha$-Fe$_2$O$_3$/Fe$_3$O$_4$ heteroplasmon nanorods via the ethanol solution combustion process of ferric nitrate

Xigang Yang$^{1,2}$, Baosheng Jin$^{1,3}$, Lulu Yu$^1$, Fahua Zhu$^1$, Yueyang Xu$^{1,2}$ and Ruijiang Liu$^{1,3}$$^*$

$^1$ School of Energy and Environment, Southeast University, Nanjing 210096, People’s Republic of China
$^2$ China Energy Science and Technology Research Institute Ltd, Nanjing 210031, People’s Republic of China
$^3$ School of Pharmacy, Jiangsu University, Zhenjiang 212013, People’s Republic of China

E-mail: bsjin@seu.edu.cn and luckystar_lrj@ujs.edu.cn

Keywords: magnetic $\alpha$-Fe$_2$O$_3$/Fe$_3$O$_4$ heteroplasmon nanorods, ethanol solution combustion process, anhydrous ethanol, calcination temperature

Abstract
An ethanol solution combustion process of ferric nitrate for preparing magnetic $\alpha$-Fe$_2$O$_3$/Fe$_3$O$_4$ heteroplasmon nanorods was introduced. The influencing factors, including the solvent type and the calcination conditions, were discussed. Anhydrous ethanol was considered to be the most suitable solvent for the preparation of $\alpha$-Fe$_2$O$_3$/Fe$_3$O$_4$ heteroplasmon nanorods, and the optimal calcination time was determined to be 2 h. By changing the calcination temperature, $\alpha$-Fe$_2$O$_3$/Fe$_3$O$_4$ heteroplasmon nanorods with different phase compositions could be obtained, and the mechanism was explained in detail. The results indicated that the rapid combustion method could achieve the controlled preparation of $\alpha$-Fe$_2$O$_3$/Fe$_3$O$_4$ heteroplasmon nanorods, which provided a general preparation approach for $\alpha$-Fe$_2$O$_3$/Fe$_3$O$_4$ heteroplasmon nanomaterials.

1. Introduction
The preparation of functional nanomaterials has become a research hotspot because of their unique properties. Among them, hematite (\(\alpha\)-Fe$_2$O$_3$) and magnetite (Fe$_3$O$_4$) have attracted extensive attention. $\alpha$-Fe$_2$O$_3$ nanomaterials are chemically stable, non-toxicity, and environmental-friendly [1–3]. However, its saturation magnetization (Ms) is low, which requires solving the recycling of materials [4]. And pure $\alpha$-Fe$_2$O$_3$ has poor electrical conductivity and sluggish surface kinetics, which limit its application [5]. Nanoscale Fe$_3$O$_4$ is widely used in catalysis, sensors, biomedical fields, owing to its good biocompatibility and unique electromagnetic properties [6–8]. Nevertheless, the magnetic Fe$_3$O$_4$ nanomaterials are in a high energy state, which are prone to agglomeration and are easily oxidized.

Heteroplasmon nanomaterials are obtained by combining inorganic materials of different properties into the same particle [9]. With the deepening of the research, it is found that the heteroplasmon nanocomposites can realize functional integration or provide new properties through the coupling of different components, thus solving the functional limitations of single-component nanomaterials [10]. For example, electric fields and voltages could manipulate the magnetic properties of $\alpha$-Fe$_2$O$_3$/Fe$_3$O$_4$, which don’t occur in pure $\alpha$-Fe$_2$O$_3$ and Fe$_3$O$_4$ [11]. Fe$_3$O$_4$/$\alpha$-Fe$_2$O$_3$ core–shell structures exhibit better photocatalytic performance than $\alpha$-Fe$_2$O$_3$ nanoparticles and can be magnetically recycled [5]. What’s more, the $\alpha$-Fe$_2$O$_3$/Fe$_3$O$_4$ heteroplasmon nanocomposites have potential applications in photocatalysis, electrochemistry, dye adsorption, drug loading, and other fields [12–15]. Therefore, it is of great significance to prepare $\alpha$-Fe$_2$O$_3$/Fe$_3$O$_4$ heteroplasmon nanocomposites with crystal uniformity and ideal composition.

On the preparation of $\alpha$-Fe$_2$O$_3$/Fe$_3$O$_4$ nanocomposites. However, most of them are nanoparticles, there are few researches on the preparation of $\alpha$-Fe$_2$O$_3$/Fe$_3$O$_4$ nanorods. Liu et al [11] obtained $\alpha$-Fe$_2$O$_3$/Fe$_3$O$_4$ nanorods by vacuum annealing, Long et al [16] prepared Fe$_3$O$_4$/$\alpha$-Fe$_2$O$_3$ nanorods on stainless steel plates,
oxygen was removed by nitrogen protection. These techniques are usually difficult to be controlled and high energy consumption. To overcome the disadvantages of other methods, a facile and safe preparation method for the preparation of \( \alpha \)-Fe\(_2\)O\(_3\)/Fe\(_3\)O\(_4\) heteroplasmon nanorods was proposed, namely the ethanol solution combustion process of ferric nitrate, which has the advantages of easy operation, low cost, environmental protection, convenience to industrialization, short fabrication period.

Herein, we prepared magnetic \( \alpha \)-Fe\(_2\)O\(_3\)/Fe\(_3\)O\(_4\) heteroplasmon nanorods via the ethanol solution combustion process of ferric nitrate, and the influences of solvent types, calcination conditions on crystal structure, phase composition, and magnetic properties were investigated to realize the controllable preparation of magnetic \( \alpha \)-Fe\(_2\)O\(_3\)/Fe\(_3\)O\(_4\) heteroplasmon nanorods.

2. Experimental

8.080 g Fe(NO\(_3\))\(_3\)\( \cdot \)9H\(_2\)O was added in 15 ml alcohol solvent. Then, the mixture was stirred for 2 h using the magnetic stirrer at room temperature. The obtained homogeneous solution was ignited. The precursor was obtained after the solution was completely burned. After that, the precursor was calcined in an air atmosphere. Finally, the magnetic \( \alpha \)-Fe\(_2\)O\(_3\)/Fe\(_3\)O\(_4\) heteroplasmon nanorods were collected by grinding the calcined products.

3. Results and discussion

3.1. Characteristics of \( \alpha \)-Fe\(_2\)O\(_3\)/Fe\(_3\)O\(_4\) heteroplasmon nanorods

SEM (figure 1(a)) and TEM (figure 1(b)) were employed to examine the morphologies of the \( \alpha \)-Fe\(_2\)O\(_3\)/Fe\(_3\)O\(_4\) heteroplasmon nanorods prepared with 15 ml ethanol and calcined at 400 °C. The average diameter of the rod-shaped structures with uniform morphologies was about 8 nm, and the average lengths up to 34 nm. As can be seen from the EDS spectra in figure 1(c), the nanorods were only composed of iron and oxygen elements, and there was no impurity residue. The percentage of iron element was 42.34%, which was between pure \( \alpha \)-Fe\(_2\)O\(_3\) (40%) and pure Fe\(_3\)O\(_4\) (42.86%), proving the existence of two phases. Figure 1(d) showed the BET specific surface areas were 19.3 m\(^2\) g\(^{-1}\), and the pore volume was 0.131 cm\(^3\) g\(^{-1}\). Figure 1(e) showed the TG-DSC curves of magnetic \( \alpha \)-Fe\(_2\)O\(_3\)/Fe\(_3\)O\(_4\) heteroplasmon nanorods, it could be divided into three weight loss stages. The weight loss of 4.59% occurred below 100 °C was assigned to the evaporation of water absorbed by the material, with an endothermic peak at 53.2 °C [17]. The major weight loss of 13.07% occurred from 100 °C to 400 °C with an exothermic peak at 261 °C, which could be attributed to the decomposition of NO\(_3\)\(^-\) [18], corresponding to the FTIR results (figure 4(e)). A slight mass loss was in the range of 400 °C to 800 °C with an exothermic peak at 467.6 °C, which could be ascribed to the combustion decomposition of the few carbon skeletons remaining in the materials [18].
Photoluminescence (PL) could explore the optical properties of the material. The PL spectra of the magnetic α-Fe₂O₃/Fe₃O₄ heteroplasmon nanorods with the excitation wavelength of 226 nm was shown in figure 2(a). A strong ultraviolet emission peak was detected at 387 nm, which may be attributed to the excitonic PL. The excitonic PL spectrum was mainly caused by oxygen vacancies and defects on the surface of the material. Small size nanomaterials had more oxygen vacancies and defects, leading to high exciton generation probability and strong PL signal [19, 20]. The Raman spectrum was shown in figure 2(b) to further confirm the structural composition of the heteroplasmon nanorods. The peaks at 222 cm⁻¹, 288 cm⁻¹, 411 cm⁻¹, 489 cm⁻¹, 608 cm⁻¹ were attributed to α-Fe₂O₃, and the peak at 670 cm⁻¹ was attributed to Fe₃O₄ [12], which proved that α-Fe₂O₃ phase and Fe₃O₄ phase exist in the heteroplasmon nanorods.

Figure 2. Photoluminescence spectra (a) and Raman spectra (b) of magnetic α-Fe₂O₃/Fe₃O₄ heteroplasmon nanorods prepared with 15 ml anhydrous ethanol and calcined at 400 °C for 2 h.

Figure 3. XRD patterns (a) and M-H curves (b) of magnetic α-Fe₂O₃/Fe₃O₄ heteroplasmon nanorods prepared by different solvents calcined at 400 °C for 2 h. XRD patterns (c) and M-H curves (d) of magnetic α-Fe₂O₃/Fe₃O₄ heteroplasmon nanorods calcined at 400 °C for different times with 15 ml anhydrous ethanol.
3.2. Influence of key factors on $\alpha$-Fe$_2$O$_3$/Fe$_3$O$_4$ heteroplasmon nanorods

Figures 3(a), (b) showed the XRD patterns and hysteresis loops (M-H curves) of the $\alpha$-Fe$_2$O$_3$/Fe$_3$O$_4$ heteroplasmon nanorods prepared with different solvents. Although the Ms of $\alpha$-Fe$_2$O$_3$/Fe$_3$O$_4$ heteroplasmon nanorods prepared using n-butanol as a solvent was 195.8 Am$^2$ kg$^{-1}$, due to the long carbon chain of n-butanol, the solubility of ferric nitrate was poor, leading to a lot of impurities in the combustion process, and low yield. When the solvent was methanol and isopropanol, the Ms were small, which was not conducive to the recovery by the external magnetic field. The Ms of anhydrous ethanol as solvent was 57.8 Am$^2$ kg$^{-1}$, while that of n-propanol as solvent was 62.66 Am$^2$ kg$^{-1}$. Considering its non-toxicity, low cost, and good performance, anhydrous ethanol was the most suitable solvent.

The effects of calcination time were investigated (figures 3(c), (d)). The shape of the diffraction peaks changed not significantly, but the intensity of the diffraction peaks changed greatly with the extension of calcination time, indicating that the calcination time mainly affected the growth degree of the crystals under the

Figure 4. XRD patterns (a), M-H curves (b), (c), phase percentages of $\alpha$-Fe$_2$O$_3$ and Fe$_3$O$_4$ (d), FTIR spectra (e) of magnetic $\alpha$-Fe$_2$O$_3$/Fe$_3$O$_4$ heteroplasmon nanorods prepared with 15 ml anhydrous ethanol and calcined at different temperatures for 2 h.
constant calcination temperature. As shown in figure 3(d), the Ms raised with the calcination time and then decreased, and the maximum Ms was 57.5 Am² kg⁻¹ at 2 h. Oxidation was inevitable as the calcination time was extended, so the Ms decreased when calcination time was more than 2 h.

Figure 4(a) displayed the XRD patterns of magnetic α-Fe₂O₃/Fe₃O₄ heteroplasmon nanorods calcined at various temperatures and the standard patterns of Fe₃O₄ (JCPDS No. 19-0629) and α-Fe₂O₃ (JCPDS No. 33-0064). The XRD patterns showed peaks at 2θ of 24.1°, 33.2°, 35.6°, 40.9°, 49.5°, which were consistent with the standard card of α-Fe₂O₃ (JCPDS No. 33-0064), confirming the existence of α-Fe₂O₃ phase at each calcining temperature. With the increase of calcination temperature, the intensity of the diffraction peak of the Fe₃O₄ phase at 2θ of 30.1° (JCPDS No. 19-0629) decreased to disappear. It revealed that the increase in temperature caused the oxidation degree of the nanorods to deepen and the phase transition from Fe₃O₄ to α-Fe₂O₃ could be realized by changing the calcination temperature.

The phase percentages of α-Fe₂O₃ and Fe₃O₄ in Fe₃O₄/Fe₂O₃ heteroplasmon nanorods were shown in figure 4(d). The phase proportions of Fe₃O₄ in nanorods calcined at 200 °C and 300 °C were 42.9% and 43.5%, respectively. And the corresponding Ms was 126.3 Am² kg⁻¹ and 127.0 Am² kg⁻¹, respectively (figure 4(b)). The increase of calcination temperature lead to the conversion of Fe₃O₄ into α-Fe₂O₃, resulting in the decrease of magnetic properties. When the calcination temperature reached 400 °C, the phase ratio of Fe₃O₄ decreased to 9.6%, and the Ms of α-Fe₂O₃/Fe₃O₄ heteroplasmon nanorods decreased to 57.5 Am² kg⁻¹. When the temperature was equal to and higher than 450 °C, the pure α-Fe₂O₃ nanocrystals were obtained with good crystallinity, and low Ms (figure 4(c)). The above results indicated that the target phase ratio nanorods could be obtained by controlling the calcination temperature.

Figure 4(e) showed the FTIR spectra of precursors and nanorods prepared at different calcination temperatures. A broadband appeared at 3400 cm⁻¹ belonged to the stretching vibration of O–H. A weak band at 1640 cm⁻¹ was assigned to H–O–H [21]. A band at 1382 cm⁻¹ corresponded to NO₃⁻, which gradually disappeared with the increase of calcining temperature and disappeared at 400 °C, indicating that the NO₃⁻ was completely removed. The characteristic bands at 462 cm⁻¹ and 551 cm⁻¹ belonged to Fe–O [22].

4. Conclusions

An ethanol solution combustion process of ferric nitrate had developed to prepare magnetic α-Fe₂O₃/Fe₃O₄ heteroplasmon nanorods. Anhydrous ethanol was the most suitable solvent, and the calcination time was determined to be 2 h. The influence mechanism of calcination temperature was described in detail. When the calcination temperature was 200 °C–400 °C, the products were typical magnetic α-Fe₂O₃/Fe₃O₄ heteroplasmon nanorods; and with the increase of temperature, the proportion of Fe₃O₄ in α-Fe₂O₃/Fe₃O₄ heteroplasmon nanorods decreased from 43.5% to 9.6%. The control preparation of α-Fe₂O₃/Fe₃O₄ heteroplasmon nanorods was realized.

Acknowledgments

This work was supported by the Science and Technology Innovation Project of CHN Energy (Grant No. GJNY-20-109).

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

ORCID iDs

Ruijiang Liu ORCID iD https://orcid.org/0000-0002-0716-832X

References

[1] Muruganandham M, Amutha R, Sathish M, Singh T S, Suri R P S and Sillanpää M 2011 Facile fabrication of hierarchical α-Fe₂O₃: self-assembly and its magnetic and electrochemical properties J. Phys. Chem. C 115 18164–73
[2] He S, Yan C, Chen X Z, Wang Z, Ouyang T, Guo M L and Liu Z Q 2020 Construction of core–shell heterojunction regulating α-Fe₂O₃ layer on Co₃O₄ nanotube arrays enables highly efficient Z-scheme photocatalysis Appl. Catal. B-Environ. 276 119138
[3] Ahmadi E, Shokri B, Mesdaghinia A, Nabizadeh R, Khani M R, Yousefzadeh S, Salehi M and Yaghmaeian K 2020 Synergistic effect of α-Fe₂O₃-TiO₂ and Na₂S₂O₈ on the performance of a non-thermal plasma reactor as a novel catalytic oxidation process for dimethyl phthalate degradation Sep. Purif. Technol. 250 117185
[4] Pan S, Huang W, Li Y, Yu L L and Liu R J 2020 A facile diethyl-carbonate-assisted combustion process for the preparation of the novel magnetic α-Fe2O3/Fe3O4 heterostructure nanoparticles Mater. Lett. 262 127071

[5] Li N, He Y L, Yi Z Z, Gao L, Zhai R and Chattopadhyay K 2020 Multiple-metal-doped Fe2O3@Fe3O4 nanoparticles with enhanced photocatalytic performance for methyl orange degradation under UV/solar light irradiation Chem. Int. Lett. 46 19038–45

[6] Gandha K, Mohapatra J, Hossain M K, Elkins K, Poudyal N, Rajeshwar K and Liu J P 2016 Mesoporous iron oxide nanowires: synthesis, magnetic and photocatalytic properties RSC Adv. 6 90537–46

[7] Saeed M S, Seyed-Yazdi J and Hekmatara H 2020 Fe2O3/Fe3O4/PANI/MWCNT nanocomposite with the optimum amount and uniform orientation of Fe2O3/Fe3O4 NPs in polyaniline for high microwave absorbing performance J. Alloy. Compd. 843 156952

[8] Yang F, Hu X, Gao S Y, Liu X F, Zhou S J and Kong Y 2020 Enabling synchronous activation of inner-core and mesoporous outer-shell of monodisperse Fe2O3@SiO2 by in situ implanted MnOx to synergistically deliver enhanced catalytic activity J. Alloy. Compd. 842 155817

[9] Cozzoli P D, Pellegrino T and Manna L 2006 Synthesis, properties and perspectives of hybrid nanocrystal structures Chem. Soc. Rev. 35 1195–208

[10] Tian Y, Wu D, Jia X, Yu B B and Zhan S H 2011 Core–shell nanostructure of α-Fe2O3/Fe3O4: synthesis and photocatalysis for methyl orange J. Nanomater. 2011 837123

[11] Liu W K, Cheng B, Xiao T T, Xie J H, Liu L, Si J R, Zhou G J, Qin H W and Hu J F 2019 Room temperature electric field control of magnetic properties for the α-Fe2O3/Fe3O4 composite structure J. Magn. Magn. Mater. 491 165500

[12] Leduc J, Goenuelle Y, Ghomgosar P, You S J, Mouzon J, Choi H, Vomiero A, Grosch M and Mathur S 2019 Electronically-coupled phase boundaries in α-Fe2O3/Fe3O4 nanocomposite photoanodes for enhanced water oxidation ACS Appl. Nano Mater. 2 334–42

[13] Zhang L, Huang Z, Shao H P, Li Y and Zheng H 2016 Effects of γ-Fe2O3 on γ-Fe2O3/Fe3O4 composite magnetic fluid by low-temperature low-vacuum oxidation method Mater. Design. 105 234–9

[14] Mohamed M M, Bayoumy W A, Goher M E, Abdo M H and El-Ashkar T Y M 2017 Optimization of α-Fe2O3@Fe3O4 incorporated N-TiO2 as super effective photocatalysts under visible light irradiation Appl. Surf. Sci. 412 668–82

[15] Liu R J, Pan S, Liu M, Huang W, Li Z X and He A L 2021 A label-free electrochemical biosensor with magnetically induced self-assembly for the detection of CYP2C9 gene Appl. Surf. Sci. 537 147668

[16] Long X Z, Gao X, Wang C Q, Liu S T and Li X N 2019 Preparation of needle-like Fe3O4/Fe2O3 nanorods on stainless steel plates to form inexpensive, high-performance bioanodes J. Electroanal. Chem. 855 113497

[17] Cheng Z X, Dong X B, Pan Q Y, Zhang J C and Dong X W 2006 Preparation and characterization of In2O3 nanorods Mater. Lett. 60 3137–40

[18] Zong M, Huang Y, Ding X, Zhang N, Qu C H and Wang Y I 2014 One-step hydrothermal synthesis and microwave electromagnetic properties of RGO/CoFe2O4 composite Ceram. Int. 40 6821–8

[19] Narayanan S, Vijayal J, Adinaveen T, Bousoudina M and Kennedy L J 2015 Synthesis of α-Fe2O3 sphere/rod-like nanostructure via simple surfactant-free precipitation route: optical properties and formation mechanism J. Nanosci. Nanotechnol. 15 4538–66

[20] Jing L Q, Qu Y C, Wang B Q, Li S D, Jiang B J, Yang L B, Fu W, Fu H G and Sun J Z 2006 Review of photoluminescence performance of nano-sized semiconductor materials and its relationships with photocatalytic activity Sol. Energy Mater. Sol. Cells 90 1773–87

[21] Ding Y L, Liu F T, Jiang Q H, Du B and Sun H D 2013 12-Hydrothermal synthesis and characterization of Fe3O4 nanorods J. Inorg. Organomet. Polym. 23 379–84

[22] Mohanraj K and Sivakumar G 2017 Synthesis of γ-Fe2O3, Fe3O4 and copper doped Fe3O4 nanoparticles by sonochemical method Sains Malays. 46 1933–42