Journal of Alloys and Compounds 744 (2018) 412–420

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Facile synthesis of α-Fe_2O_3 pyramid on reduced graphene oxide for supercapacitor and photo-degradation

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ARTICLE INFO

Article history:
Received 21 April 2017
Received in revised form
20 November 2017
Accepted 11 February 2018
Available online 13 February 2018

Keywords:
α-Fe_2O_3
Reduced graphene oxide
Supercapacitor
Photo-degradation

ABSTRACT

We report a novel method to synthesize a novel α-Fe_2O_3 pyramid interspersed reduced graphene oxide composite by continuous 20-second flame treatment. The structural and morphological characteristics of the obtained composites were investigated by Fourier transform infrared spectroscopy, X-ray diffraction, energy dispersive X-ray spectroscopy, X-ray photoelectron spectroscopy, Raman spectrum, and Field-emission scanning electron microscopy. Pyramid-type α-Fe_2O_3 is found to be successfully decorated on reduced graphene oxide. Such a unique composite not only gives a high specific capacitance (965.7 F/g at 5 mV/s) and a good cycling performance, but also shows a strong, stable photo-degradation capacity of Rhodamine-B under simulation solar light (with 100% of degradation rate within 10 min). It is worthy of note that the content of graphene oxide in precursors is found to highly affect the formation of the crystal structure of α-Fe_2O_3, thus intensely affecting the electrochemical behaviors and photo-degradation capacity.

1. Introduction

Continuous scientific efforts have been made to focus on the optimization of α-Fe_2O_3 by modulating its electrochemical properties and structural characteristics, such as conductivity, morphology, size, defect, active site, *etc.* in order to promote its applications in practice including energy storage [1–5], and photocatalysis [6–8]. Currently, mainstream methods including hydrothermal [9,10], and solvothermal [1,2] method along with others such as MOF calcination [11] were developed to synthesize α-Fe_2O_3. Some unique structures such as 2D hexagonal nanoplate [6], nanorod [7], nanotube [12], nanodot [5], tetrakaidecahedron [8], nanocube [13], ellipsoid shape [14] and hyperbranched structure [15] were successfully synthesized by the above-mentioned methods and their modifications. It is found that efficient charge transfer and more contact active sites are the key factors to lead to an enhanced performance in semiconductor nanocomposites such as these of α-Fe_2O_3-related materials [16]. Particularly, 2D hexagonal nanoplate, tetrakaidecahedron, and nanocube with more edges and horns showed more unique, excellent performances such as in energy storage, photodegradation, water splitting, *etc.* Therefore, such unique structure can be benefit for improving charge transfer and contact active sites. Nevertheless, only a few works in terms of this field have been reported because of its anfractuous configuration. Among them, S. Bharathi et al. found that α-Fe_2O_3 nanocube showed a stronger photodegradation than those of nanostructured dendrites, nanorods, and nanospindles [13]. α-Fe_2O_3 with 2D hexagonal nanoplate synthesized by Fang' group shows an excellent photocatalytic activity due to a better contact with graphene [6]. Cubical and rhombic α-Fe_2O_3 nanoparticles decorated on N-doped graphene as supercapacitor electrode materials showed a high specific capacitance of 618 F/g at 0.5 A/g [9]. Furthermore, Wang, et al. found that hydrothermal α-Fe_2O_3 cube reached an ultrahigh specific capacitance up to 908 F/g at 2 A/g [10]. Recently, Fang' group synthesized α-Fe_2O_3 tetrakaidecahedron, giving a superior photocurrent response [8]. Therefore, design and synthesis of α-Fe_2O_3 with many edges and horns is quite important for the practical applications.

In this work, we report a novel method to synthesize a novel composite consisting of α-Fe_2O_3 with numerous edges and horns,

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https://doi.org/10.1016/j.jallcom.2018.02.126
0925-8388/

and reduced graphene oxide (defined as α-Fe_2O_3/rGO) by 20-second flame treatment. The structural and morphological characteristics of the obtained composites were investigated by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), Raman spectrum, and Field-emission scanning electron microscopy (FE-SEM). Results show that pyramid-type α-Fe_2O_3 interspersed on the surface of rGO sheets was successfully synthesized. To the best of our knowledge, this is the first time to synthesize such a unique morphology of pyramid shape. The electrochemical behaviors describe a high specific capacitance (965.7 F/g at 5 mV/s) and a good cycling performance. Not only this, it also shows a strong, stable photo-degradation capacity of Rhodamine-B (RB) (with 100% of degradation rate within 10 min). Moreover, our findings shows that increasing the content of GO in precursors can obviously weaken the crystal structure of α-Fe_2O_3, leading to a weaker specific capacitance and photo-degradation capacity. To conclude, this work shows the potential to prepare graphene-related metal oxide composites with good performances for applications in energy storage and water treatment.

2. Experimental sections

2.1. Reagents

Natural flake graphite (Qingdao Jinrilai graphene corporation), $NaNO_3$ (Chengdu Kelong reagent factory, AR), $KMnO_4$ (Chongqing Chuandong chemical (group) CO., LTD, AR), 30% of hydrogen peroxide (Chengdu Kelong reagent factory, AR), 98% of H_2SO_4 (Chongqing Chuandong chemical (group) CO.,LTD, AR), $FeCl_3 \cdot 6H_2O$ (Chengdu Kelong reagent factory, AR), Rhodamine-B (Chengdu Kelong reagent factory, AR), KOH (Chengdu Kelong reagent factory, AR), Ethanol (Chengdu Kelong reagent factory, AR).

2.2. Synthesis of graphite oxide (GtO)

Here modified Hummers' method was employed to synthesize GtO, and the detailed procedures see the as-reported work [17].

2.3. Synthesis of α-Fe_2O_3/rGO

α-Fe_2O_3/rGO was synthesized by a continuous 20-second flame treatment from an alcohol lamp with absolute ethyl alcohol as bunkers. To strictly control the whole process, windless room and proper reaction distance were necessary to ensure that the flame could fully react with the sample. To prepare the precursor $FeCl_3$/GO composites, 0.5 g of $FeCl_3 \cdot 6H_2O$ and 0.5 g of GtO was added into 50 mL of distilled water and sonicated for 1 h. After that, the obtained mixture was placed on a surface dish, and dried at 50 °C for 24 h to obtain $FeCl_3$/GO papers. A random $FeCl_3$/GO paper was placed on steel net where the steel net has a fixed distance to an alcohol lamp. After that, the lamp was lighted and quenched after 20 s. In the end, the brownish black paper turned into kermesinus, loose solid. The ultimate products are α-Fe_2O_3/rGO.

2.4. Electrochemical measurements

All electrochemical processes were carried out on a CHI600D electrochemical workstation (Shanghai Chenhua, China) by a three-electrode system in 2 M KOH aqueous solution. The obtained α-Fe_2O_3/rGO was pressed into two foam nikel plates at 8 Mpa to obtain the working electrode. Pt sheet and saturated calomel electrode (SCE) as counter and reference electrodes were used, respectively. The cyclic voltammetry (CV) behavior was conducted at different scan rates of 5–200 mV with the potential window from −0.15–0.55 V. Galvanostatic charge/discharge behavior was performed with the potential range from 0 to 0.4 V at various current densities of 0.5–5 A g^{-1}. Electrochemical resistance spectroscopy (EIS) was carried out in the frequency range of 0.01–10^6 Hz. For every sample, the average mass loaded on the electrode is about 2.5 mg.

2.5. Heterogeneous photo-Fenton degradation of RB

The photo-catalytic activity of the as-prepared α-Fe_2O_3/rGO was evaluated by the removal of RB under the illumination (a 300 W Xe lamp). All photo-catalytic experiments were conducted in a 250 mL of beaker with constant magnetic stirring at ambient temperature. For the degradation of RB, 10 mg of the as-prepared composites were added to 15 mg/L of RB aqueous solution, and before illumination, the mixture was stirred for 30 min to reach the absorption-desorption equilibrium in the sufficient dispersion of the catalyst. 0.5 mL of H_2O_2 ($\geqq$30%) solution was added to the mixture before photoreaction. About 4 mL of the mixture was collected after given irradiation time intervals, centrifuged and analyzed by detecting the absorbance of RB at 550 nm.

2.6. Physical measurements

Fourier transform infrared spectroscopy (FT-IR) was collected on a Nicolet iS50 spectrometer from 4000 to 400 cm^{-1}. X-ray diffraction (XRD) patterns were obtained by a PANalytical X'Pert powder. Field-emission scanning electron microscopy (FE-SEM) and energy dispersive X-ray spectroscopy (EDS) was performed on a FEI NanoSEM 450. X-ray photoelectron spectroscopy (XPS) were collected on a Thermo Scientific K-Alpha. Raman spectra were obtained by a LabRAM HR Evolution spectrophotometer. Photoluminescence emission spectra were obtained by a Cary Eclipse (American).

3. Results and discussion

In this work, a novel α-Fe_2O_3 pyramid decorated rGO composite was successfully synthesized by flame treatment including three main stages. As shown in Scheme 1, $FeCl_3$ was firstly intercalated into between rGO layers to form the intercalated composites. Secondly, during flame treatment, bad-thermal-conductivity GO rapidly decomposed into rGO with good thermal conductivity, accompanied by a lot of gases and heat released. At last, $FeCl_3$ in-situ decomposed into Fe_2O_3 on the surface of rGO to obtain α-Fe_2O_3/rGO composites. It is highlighted that rGO acts as a thermal conductor, thus benefit for the decomposition of $FeCl_3$ into α-Fe_2O_3, and improve the conductance of α-Fe_2O_3 to promote electron-hole separation in energy storage and photodegradation.

As shown in Fig. 1A(b-c), all of the obtained α-Fe_2O_3/rGO materials show typical characteristic peaks of α-Fe_2O_3, as evidenced by the standard card JCPDS 33-0664 with the lattice parameters of $a = 5.04$, $b = 2.49$, and $c = 13.76$ Å [4,6]. The peaks were observed at 24.0°, 33.3°, 35.7°, 41°, 43.4°, 49.6°, 54.2°, 57.2°, 62.6°, and 64.1°, corresponding to (012), (104), (110), (113), (202), (024), (116), (018), (214), and (300) crystal planes of α-Fe_2O_3, respectively [4,8]. Moreover, a peak at 30.3° shown indicates the presence of γ-Fe_2O_3 [18]. γ-Fe_2O_3 with a smaller particle size has been reported to have a thermally more stable than α-Fe_2O_3 [14]. This was observed in SEM images, where α-Fe_2O_3/rGO from 60% GO in precursors shows more small sphere particles. Relatively, α-Fe_2O_3/rGO composites from 50% GO and 75% GO in precursors both show obviously a lower peak intensity. An obviously broad peak at 26.2° appears, suggesting the presence of rGO, which is consistent with the pure rGO, as observed in Fig. 1A(a) [4,19]. Differently, the peak site in