Journal of Alloys and Compounds 671 (2016) 552–559

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

Synthesis, exploration of energy storage and electrochemical sensing properties of hematite nanoparticles

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ARTICLE INFO

Article history:
Received 28 October 2015
Received in revised form
18 January 2016
Accepted 6 February 2016
Available online 9 February 2016

Keywords:
Hematite nanoparticles
Gel-combustion
Solution combustion
Molten salt method
Lithium-ion battery
Dopamine sensor

ABSTRACT

Gel-combustion, solution combustion and molten salt methods were used to synthesize hematite nanoparicles. Two weight ratios of precursor (Ferric nitrate) to fuel (Cassava Starch) (1:0.5, 1:1) were used in gel-combustion technique. Ferric nitrate as a precursor and ethylenediamine tetraacetic acid as fuel (in stoichiometric proportions) were used in the solution combustion method. Ferric oxalate was the precursor in molten salt method. The structural parameters of the hematite nanoparticles were studied by X-ray diffraction. The optical properties, including band gap studies were done by UV–Visible spectroscopy. The morphological studies were carried out by Scanning Electron Microscope. The energy storage capacity of the molten salt method-hematite nanoparticles surpassed (920 $mAhg^{-1}$) the others while the equal-weight- ratio-hematite nanoparticles synthesized by gel-combustion method exhibited better dopamine sensor properties.

1. Introduction

Nanotechnology harnesses current progress in chemistry, physics, material science to create materials with unique properties and structures. In recent years, tremendous interest has been devoted to the study of metal oxides nanoparticles, especially, semiconductor transition metal oxides like ZnO, CuO, NiO, Fe_2O_3, Co_3O_4, V_2O_5, etc due to their application in the fields of photocatalysis [1], magnetic devices [2], microelectronics [3], alternative energy sources [4,5], bio medical devices [6]. Amongst the transition metal oxides, iron oxide nanostructures have attracted attention due to their magnetic, electrical optical and chemical properties [7]. Though multiple phases of iron oxide exists, obtaining only one type of phase is very useful in advanced applications. Hematite, an anti-ferromagnetic and an important form of iron oxide, is environmentally friendly with a band gap of 2.2 eV (n-type and indirect semiconductor) and can be used for various applications [7]. They include waste water treatment [8], antimicrobial activity [9], photoelectrochemical water splitting [4], electrode material for lithium ion batteries [10], photocatalytic degradation [11], chemical [12] and electrochemical sensing [13]. With increasing energy crisis, there is a wide-spread search for energy storage materials and hematite finds a lot of application in lithium ion batteries as anode material [14,15]. Hematite is studied in the form of nanotubes [16], multi-shelled hollow microspheres [17], mesoporous nanostructures [18], nanoflakes [19], nanofibres [20] composite along with carbon nano tubes [21] and graphene [20,22] as an effective anode material.

Fe_2O_3 was previously considered biologically and chemically inert. Hence, the electrochemical characterization as well as sensing was paid little attention [23]. Recently, hematite finds application in electrochemical sensing of folic acid [24],ethanol [25] and dopamine (DA) [13,26] because of its low cost, small dimension and convenient operation [27]. DA, a biologically important chemical messenger, sends signals from the brain to different parts of the body. Any abnormality in DA produced by the central nervous system is a sign of neurological disorder and moreover, it is also closely linked with the pleasure and reward centre of the brain [28]. This important neurotransmitter has been detected by various established analytical methods which include capillary electrophoresis, high performance liquid chromatography coupled with mass spectrometry, spectrophotometry, etc. [29-31] Though these

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http://dx.doi.org/10.1016/j.jallcom.2016.02.050
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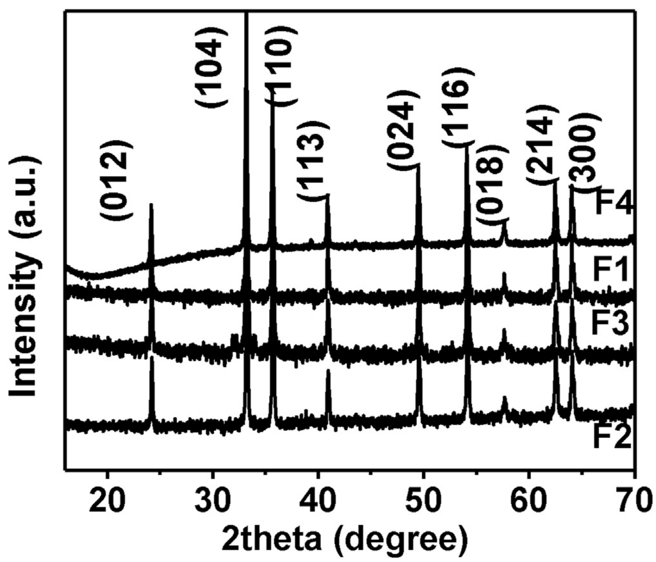

Fig. 1. X-Ray Diffraction patterns of Hematite powder samples.

methods are highly sensitive, yet they are quite complex, time-consuming and costly. However, electrochemical detection is simple, fast, cheap, selective as well as sensitive [32-34]. There are quite a few reports in the literature on the synthesis, structural and morphological properties of hematite nanostructures. It can be synthesised by sonochemical [35], hydrothermal [17], hydrothermal emulsion polymerization [22], thermal treatment [19], solid state chemical reaction using $FeCl_3$ as precursor [36], template synthesis using co-polymer surfactant F127 [18], using polysaccharide template [37] and by sol gel methods [38]. Hematite nanostructures have also been prepared by combustion techniques which have advantages over the other methods of synthesis due to its simple and rapid preparation process [39]. The advantages of combustion techniques are: (1) the quasi-atomic dispersion of the component cations in liquid precursors, which facilitates synthesis of crystallized powder with low particle size and high purity at relatively low temperatures [40], (2) it is a single step solvent-free process, (3) continuous and not a batch process that is intrinsically stable [41], (4) it is a self-sustaining, self-propagating and highly exothermic reaction. The exothermicity makes the reaction special as well as attractive [42]. Dhoman and coworkers have used glycine as a fuel [43], while Prabhu et al. [44] have used glycine and TWEEN 80 as a non-ionic surfactant to prepare α-Fe_2O_3 by combustion technique. α-Fe_2O_3 was synthesized by a mixture of fuels like hydrazine, glycine and citric acid by Deshpande et al. [45] Of late, utilization of non-toxic and environmentally benign precursors and fuels are the key to many synthesis strategies. Starch is a natural polymer rich in carbohydtates and has been used as a single and combined fuel with N-methyl urea by Visinescu et al. [46] and by Bai et al. [47] as one of the fuels in the mixture of urea and glycine to synthesise zinc aluminium oxide and $MgAl_2O_4$ powders, respectively. Molten salt synthesis has also been undertaken by many researchers to obtain high crystalline product. It is a solvent-free process where low-melting salts like alkali chlorides and hydroxides accelerate diffusion and formation of required structure in a single step [48]. To ensure maximum reactivity of the medium at minimal temperature, combination of suitable salts were used as eutectic mixture [49]. By this method various binary CuO [50], MO_2 (M = Ti, Sn) [51-53], ternary oxides (MCo_2O_4, M = Co, Zn, Cu, Mn) [54-56] and other mixed oxides [57-60] have been prepared and its physical and electrochemical properties were studied.

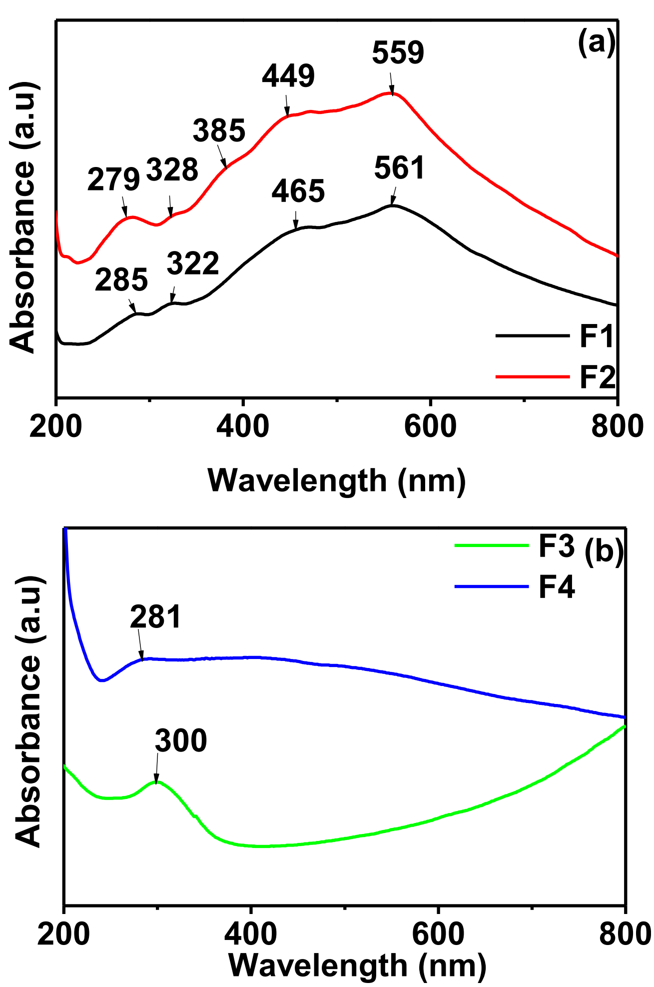

Fig. 2. UV–Visible Spectra of hematite samples (a) F1, F2 and (b) F3, F4.

In this paper, four samples of hematite have been synthesized by gel-combustion, solution combustion, and molten salt methods and experimented for energy storage and electrochemical sensing applications. A modified form of starch prepared from processed tubers of cassava plant and ethylene diaminetetraacetic acid (EDTA) and have been used as fuel for gel-combustion synthesis and solution combustion synthesis, respectively. Cassava (*Manihot esculenta*, scientific name) belongs to Euphorbiaceae family. It is an important staple crop of the arid tropics which is rich in starch content [61].

2. Experimental procedure

2.1. Preparation of fuels

2.1.1. Preparation of cassava starch

A known weight of cassava pearls (purchased from local market) were cleaned to remove solid impurities, washed with tap water to remove suspended impurities and rinsed with distilled water. Known volume of water was added to the cassava pearls and heated on a hot plate at 200 °C till the pearls were transparent and gel-like. It was cooled and transferred to a clean plastic sheet, covered with a thin cloth to prevent dust contamination and exposed to bright sunlight for a week. The sun-dried products were powdered and stored in an air-tight container to prevent infestation. This was known as “Cassava Starch”. This procedure was developed by our group [62].