Analytica Chimica Acta xxx (2018) 1–8

Contents lists available at ScienceDirect

Analytica Chimica Acta

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

# Electrospun γ-$Fe_2O_3$ nanofibers as bioelectrochemical sensors for simultaneous determination of small biomolecules

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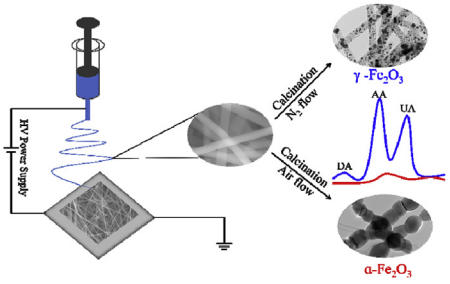
## HIGHLIGHTS

- The structure of $Fe_2O_3$ nanofibers can be easily adjusted assisted by electrospinning.
- γ-$Fe_2O_3$ nanofibers show excellent electrocatalytic performances toward biomolecules.
- α-$Fe_2O_3$ nanofibers display no obvious electrocatalytic activities.

## GRAPHICAL ABSTRACT




## ARTICLE INFO

*Article history:*
Received 24 December 2017
Received in revised form
20 March 2018
Accepted 2 April 2018
Available online xxx

*Keywords:*
$Fe_2O_3$
Electrospuning
Nanofiber
Electrocatalysis
Dopamine

## ABSTRACT

Nanofibers of α-$Fe_2O_3$ and γ-$Fe_2O_3$ have been obtained after the controlled calcination of precursor nanofibers synthesized by electrospinning. α-$Fe_2O_3$ nanofibers showed an irregular toruloid structure due to the decomposition of poly (4-vinyl) pyridine in air while γ-$Fe_2O_3$ nanoparticles decorated nanofibers were observed after the calcination under $N_2$ atmosphere. Electrochemical measurements showed that different electrochemical behaviors were observed on the glassy carbon electrodes modified by α-$Fe_2O_3$ and γ-$Fe_2O_3$ nanofibers. The electrode modified by γ-$Fe_2O_3$ nanofibers exhibited high electrocatalytic activities toward oxidation of dopamine, uric acid and ascorbic acid while α-$Fe_2O_3$ nanofibers cannot. Furthermore, the γ-$Fe_2O_3$ modified electrode can realize the selective detection of biomolecules in ternary electrolyte solutions. The synthesis of nanofibers of α-$Fe_2O_3$ and γ-$Fe_2O_3$ and their electrochemical sensing properties relationship have been discussed and analyzed based on the experimental results.



## 1. Introduction

With the development of nanoscience and technology, nanometric materials with delicate structures have been explored unique physicochemical properties that are different from the corresponding buck materials [1,2]. Either metals or metal oxide nanomaterials are important functional materials and have been developed owning to their wide applications [3,4]. As one type of important oxides, $Fe_2O_3$ has been usually used in many fields, for example, as dyes due to its unique d-d transition electronic structure and as supports for catalyts owing to the chemical inert

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https://doi.org/10.1016/j.aca.2018.04.010
0003-2670/

properties [5]. $Fe_2O_3$ usually exhibits two different structures, namely hematite ($\alpha$-$Fe_2O_3$) and maghemite ($\gamma$-$Fe_2O_3$). Hematite has a band gap of 2.3 eV and is effectively applied, for example, to photocatalysis during the last decade [6,7]. Maghemite has been successfully used in many fields, for instance, as a drug delivery carrier due to its biocompatibility and ferrimagnetic behavior [8]. Synthesis methodology has been explored to realize the controlled synthesis of hematite or maghemite nanostructures, which includes various synthesis methods, such as the hydrothermal/solvothermal method [9–11], pyrolysis [12], electrospinning [13] and electrochemical synthesis [14,15]. Electrospinning seems to provide an easy way to obtain nanofibers, which can precisely control the diameter, morphology, composition, porosity secondary structure, and spatial alignment of nanofibers to achieve desired functionalities and properties [16]. Various nanofibers have been widely used in chemical sensors, electrode materials, filtration and optical applications due to their high specific surface area, tunable porosity and reasonable ion channels [17,18]. For example, electrospun nanofibers of iron oxide give an effective approach to explore their unique electrocatalytic and energy storage performance compared with nanoparticles or bulk materials [13,19]. However, controlled synthesis of nanofibers of hematite and maghemite still needs to be further developed [20,21].

Dopamine (DA), uric acid (UA) and ascorbic acid (AA) are important biomolecules of human metabolism [22]. These three small biomolecules usually coexist in biological samples and the lack of each above molecule will arouse human disease or disorder. For instance, dopamine plays a vital role in the information transfer of the mammalian central nervous system and the lack of DA will cause many nervous diseases such as parkinsonism and senile dementia. It is essential to exploit a high selective and sensitive method for their routine determination. Voltammetry method has been proved to be a powerful technology for the detection of these small biomolecules [23–25]. However, the electrochemical reactions of the three biomolecules at bare electrodes are irreversible and require high overpotentials. The overlap of their cyclic voltammetry at bare electrodes makes it very hard to detect and reproduce selectively. AA interacts with DA strongly because AA exists as an anion while DA as a cation. Furthermore, the oxidation products of DA can effectively catalyze oxidation of AA, and thus it is difficult to accurately and selectively detect single biomolecules [26].

To overcome the above problems, a variety of electrocatalysts have been developed to improve selectivity and sensitivity, including noble metals [27], polymers [28], ferromagnetic materials [29], carbon nanotube [30], graphene [31], etc. Among them, ferromagnetic materials, such as $Fe_3O_4$ and $\gamma$-$Fe_2O_3$ nanoparticles, as well as $\alpha$-$Fe_2O_3$ nanostructures have been brought into focus in the fields of chemical and biological sensors due to their good catalytic activity and low cost [32,33]. For example, $\alpha$-$Fe_2O_3$ nanorings can be used as active electrode materials to realize the detection of $H_2O_2$ [34], $\gamma$-$Fe_2O_3$ modified electrode has been applied to the photoelectrochemical water splitting [35]. From this point of view, it is possible to explore the electrochemical sensing properties of $Fe_2O_3$ nanofibers with controlled structures.

In this work, two kinds of $Fe_2O_3$ nanofibers with maghemite and hematite structures have been synthesized controllably by electrospinning technique and post-processing, having been used for simultaneous determination of AA, DA and UA in phosphate buffer saline solution. The electrochemical behavior of these three molecules on the modified electrodes has been investigated by using cyclic voltammetry and differential pulse voltammetry. It was found that the electrode modified by $\gamma$-$Fe_2O_3$ nanofibers can realize the simultaneous electrochemical detection of AA, DA and UA with high sensitivities while $\alpha$-$Fe_2O_3$ nanofibers cannot.

## 2. Experimental

### 2.1. Materials

All the chemicals, except DA (99%) from Aldrich, were of analytical grade (purchased from Sinopharm Chemical Reagent Co. LTD), including $FeCl_3 \cdot 6H_2O$, $NaH_2PO_4$, $K_3Fe(CN)_6$, KBr, KCl, $K_4Fe(CN)_6$, UA, AA, poly (4-vinyl) pyridine (PVP, $M_w = 1{,}300{,}000$), polyethylene glycol (PEG, $M_w = 4000$), ethanol, and nitric acid (65–68 wt.%). Ultrapure water (18.2 MΩ cm) was used in all electrochemical experiments. The aqueous PBS buffer contained 0.05 M $NaH_2PO_4$ and 0.1 M KBr.

### 2.2. Synthesis of $Fe_2O_3$ nanofibers

The typical synthesis process was divided into three steps. Firstly, 0.5 g $FeCl_3 \cdot 6H_2O$ was dissolved in a mixed solution composed of 3 mL of water, 2 mL of ethanol and 0.2 mL of nitric acid. An appropriate quantity of PEG was then added, followed by the introduce of PVP up to a concentration of 8 wt. % under vigorously stirring. Then the homogenous solution was put in a 5 mL syringe with metal needle of 0.6 mm in internal diameter. Secondly, power supply (18 kV) was used to provide a direct-current electric field between the needle and Al foil collector with the ejection rate of 0.5 mL $h^{-1}$. The as-spun fibers were dried for 6 h in a vacuum at 70 °C. Finally, in order to obtain $\gamma$-$Fe_2O_3$ nanofibers, the precursor fibers were calcined through a two-step process in $N_2$ atmosphere, namely, calcined at 500 °C for 1 h with heating rate of 2 °C $min^{-1}$ and then at 800 °C for 5 h with heating rate of 5 °C $min^{-1}$. The as-obtained black $\gamma$-$Fe_2O_3$ nanofibers were named as $\gamma$-$Fe_2O_3$-NF. Red $\alpha$-$Fe_2O_3$ nanofibers named as $\alpha$-$Fe_2O_3$-NF were obtained with the same calcination process as that of $\gamma$-$Fe_2O_3$-NF except for the calcination conditions in air. The products were collected by centrifuge tube and kept dry before further characterization.

### 2.3. Characterization

The morphology and energy dispersive X-ray spectroscopy (EDS) of $\alpha$-$Fe_2O_3$-NF and $\gamma$-$Fe_2O_3$-NF were measured with a field emission scanning electron microscopy (FESEM) (JEOL JSM-7800 F). Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were obtained on the JEOL JEM2010 TEM operated at 200 kV. The crystal structures of the products were investigated by using a Rigaku Ultima IV X-ray diffractometer (XRD, Cu-K$\alpha$ radiation $\lambda = 0.15418$ nm). Raman spectra were recorded by using a Renishaw inVia Plus Micro-Raman spectroscopy system equipped with a 50 mW DPSS laser at 532 nm.

### 2.4. Electrochemical measurements

The glassy carbon electrode (GCE) surface (3 mm in diameter) was carefully polished to a mirror-like surface and cleaned before being used at room temperature. $Fe_2O_3$ nanofibers (1 mg) were dispersed in 1 mL ultrapure water by ultrasonication. Then 10 μL solution was dripped onto the clean GCE by syringe and dried in air before being used. Electrochemical measurements were conducted on a CHI760E electrochemical workstation (CH Instruments, USA) using a conventional three-electrode cell measurement method. The $Fe_2O_3$-modified electrode was used as the working electrode with a Pt foil as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode in PBS solutions.

## 3. Results and discussion

In our experiments, two types of the $Fe_2O_3$ nanofibers are

Please cite this article in press as: Q. Wang, et al., Electrospun $\gamma$-$Fe_2O_3$ nanofibers as bioelectrochemical sensors for simultaneous determination of small biomolecules, Analytica Chimica Acta (2018), https://doi.org/10.1016/j.aca.2018.04.010