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Fast ultrasound assisted synthesis of chitosan-based magnetite nanocomposites as a modified electrode sensor

T.M. Freire[a], L.M.U. Dutra[b,d], D.C. Queiroz[b], N.M.P.S. Ricardo[b], K. Barreto[b], J.C. Denardin[c], Frederik R. Wurm[d], C.P. Sousa[e], A.N. Correia[e], P de Lima-Neto[e], P.B.A. Fechine[a,*]

[a] *Group of Chemistry of Advanced Materials (GQMAT)-Department of Analytical Chemistry and Physical-Chemistry, Federal University of Ceará-UFC, Campus do Pici, CP 12100, CEP 60451-970 Fortaleza, CE, Brazil*

[b] *Department of Organic and Inorganic Chemistry, Federal University of Ceará-UFC, Campus do Pici, CP 12100, CEP 60451-970 Fortaleza, CE, Brazil*

[c] *Department of Physical, University of Santiago de Chile, USACH, Av. Ecuador 3493, Santiago, Chile*

[d] *Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany*

[e] *Group of Electrochemistry and Corrosion (GELCORR)-Department of Analytical Chemistry and Physical-Chemistry, Federal University of Ceará-UFC, Campus do Pici, CP 12100, CEP 60451-970 Fortaleza, CE, Brazil*

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ABSTRACT

Chitosan-based magnetite nanocomposites were synthesized using a versatile ultrasound assisted *in situ* method involving one quick step. This synthetic route approach results in the formation of spheroidal nanoparticles (Fe_3O_4) with average diameter between 10 and 24 nm, which were found to be superparamagnetic with saturation magnetization (Ms) ranges from 32–57 emu g^{-1}, depending on the concentration. The incorporation of Fe_3O_4 into chitosan matrix was also confirmed by FTIR and TG techniques. This hybrid nanocomposite has the potential application as electrochemical sensors, since the electrochemical signal was exceptionally stable. In addition, the *in situ* strategy proposed in this work allowed us to synthesize the nanocomposite system in a short time, around 2 min of time-consuming, showing great potential to replace convencional methods. Herein, the procedure will permit a further diversity of applications into nanocomposite materials engineering.

1. Introduction

Development of organic-inorganic nanocomposites has attracted attention of many researchers, since these materials can be applied in different areas of science. Magnetic nanoparticles (MNPs), such as magnetite (Fe_3O_4), have shown huge potential for different applications: enzyme immobilization, waste water treatment, targeted delivery of drugs and biosensors (Lim et al., 2015; Wang, Li, Luo, Wang, & Duan, 2016; Zhang et al., 2010), owing to their superparamagnetic behavior and low toxicity. However, the large surface area-to-volume ratio in Fe_3O_4 MNPs exhibits a high surface energy and they tend to aggregate, limiting their range of applications (Gregorio-Jauregui et al., 2012; Yallapu et al., 2011).

Herein, controlling and/or preventing particles agglomeration makes their production a truly challenge into industry field. Thus, organic compounds have been used to cover MNPs, promoting stability and surface functionalization (Nicolás et al., 2013; Zhang et al., 2012). Several works proved that magnetite nanoparticles coated by chitosan (Shete et al., 2014), poly(vinyl alcohol) (Mahmoudi, Simchi, & Imani, 2009), poly(acrylic acid) (Xu, Zhuang, Lin, Shen, & Li, 2013), DNA (Navarathne, Ner, Jain, Grote, & Sotzing, 2011), or proteins (Bayrakci et al., 2014Bayrakci, Gezici, Bas, Ozmen, & Maltas, 2014), promotes whether electrostatic or steric repulsion, stabilizing MNPs dispersion. Chitosan has become one of most used natural polymer, being biocompatible, biodegradable and bioactive. Additionally, this polyaminosaccharide has intrinsic chemical properties, which its free amino groups allow the formation of positively charged complexes, providing reactive sites to bind Fe-based MNPs (Shen, Shen, Wen, Wang, & Liu, 2011; Zhang et al., 2010).

Some studies have been demonstrated that nanosize and surface effects display significant rules in NP's magnetic behavior.

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* Corresponding author.
E-mail addresses: tiagomfreire.ufc@gmail.com (T.M. Freire), lmudutra@hotmail.com (L.M.U. Dutra), daniloqueiroz46@gmail.com (D.C. Queiroz), nagilaricardo@gmail.com (N.M.P.S. Ricardo), kambarreto@yahoo.com.br (K. Barreto), juliano.denardin@usach.cl (J.C. Denardin), wurm@mpip-mainz.mpg.de (F.R. Wurm), pinheiro.cs@gmail.com (C.P. Sousa), adriana@ufc.br (A.N. Correia), pln@ufc.br (P. de Lima-Neto), fechine@ufc.br (P.B.A. Fechine).

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Innumerous strategies have been developed in order to modulate a hybrid functional metal oxide with desired properties, such as co-precipitation (Silva et al., 2013), hydrothermal synthesis (Gyergyek, Drofenik, & Makovec, 2012) and sonochemistry (Barkade, Pinjari, Nakate et al., 2013; Barkade, Pinjari, Singh et al., 2013; Theerdhala et al., 2010). However, these methods are energy and time-consuming, and thus it is important to highlight the use of ultrasound for synthesis involving a wide range of nanomaterials, such as silver nanoparticles (He et al., 2014), magnesium ferrite (Chen, Li, zhang, & Kang, 2013) and iron oxide (Dolores, Raquel, & Adianez, 2015). The technique has become an easy and simple tool, that may promotes ultrahigh surface area (organic/inorganic) with synthesis of inorganic material during process (*in situ* method), which the formation of a monodisperse can tailor hybrid materials, controlling the crystal growth and forming particles with nanometer size distribution (Barkade, Pinjari, Singh et al., 2013; Carroll, Ulises-Reveles, Shultz, Khanna, & Carpenter, 2011).

In general, chitosan-based magnetite synthesis results in two types of different structures: a single magnetite core surrounded by a chitosan layer, and/or magnetite “multi-cores” dispersed in a chitosan matrix (Patil et al., 2014; Reddy & Lee, 2013; Safari & Javadian, 2015). Recently, Safari and Javadian synthesized Fe_3O_4-chitosan nanoparticles by co-precipitation method under ultrasound irradiation in two different steps. Firstly, they obtained the magnetic nanoparticles by chemical co-precipitation, followed by a subsequent functionalization with chitosan by aid of ultrasound. Even though, cavitation phenomenon provides an increase in reactions rate, the ultrasound irradiation (US) is used only in the second step. Thereby, the adapted method is still being time-consuming, since the synthesis is carried out in two sequential steps, namely particle precipitation and functionalization (Safari & Javadian, 2015).

In this work, we present a rapid ultrasonic assisted *in situ* route to produce magnetic Fe_3O_4-chitosan nanocomposites, where the chemical co-precipitation and functionalization occur at the same time, *i.e.*, in one quick step. Besides the *in situ* method synthesizes MNPs with low crystallite size, high crystallinity and saturation magnetization, the nanocomposite material has shown optimal electrochemical response due to development of modified electrodes. Furthermore, our method minimizes the oxidation of magnetite and drastically decreases the synthesis time from several minutes and/or hours for the conventional co-precipitation method to a few minutes (~2 min). Additionally, in the sense of electrochemical sensors application, the proposed route is potentially ideal to produce a large amount of material, *i.e.*, scaling up to industrial level, since sensors of hybrid materials based on chitosan and Fe_3O_4 have been developed for detection of glucose (Kaushik et al., 2008), urea (Kaushik et al., 2009) and as sensors for diseases diagnosis (Tran et al., 2011).

2. Experimental procedure

2.1. Materials

Chitosan (DPN – Delta Produtos Naturais Ltda) was characterized regarding to molecular weight (M_w), 31 kDa, and deacetylation degree (DD), 92%, by gel permeation chromatography (GPC) and potenciometry, respectively. Ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$, 97%), potassium ferrocyanide ($K_4Fe(CN)_6$, 98.5%), potassium ferricyanide ($K_3Fe(CN)_6$, 99%), potassium chloride (KCl, 99%) and glacial acetic acid (CH_3COOH, 99.7%) were purchased from VETEC. Ferrous sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$, 99%) and ammonium hydroxide solution (NH_4OH, 30%) were purchased from DINAMICA, and glutaraldehyde solution 25% from Sigma-Aldrich. All used reagents are analytical grade.

2.2. Preparation of chitosan/Fe_3O_4 nanocomposites

The magnetic chitosan nanocomposites were synthesized as follow. Firstly, different amounts of chitosan (0.1, 0.05 and 0.01 g) were dissolved in 15 mL of acetic acid 1% (v/v) under stirring at 50 °C for 10 min. Subsequently, 10 mL of Fe solution 0.33 mol L^{-1} ($FeCl_3.6H_2O/FeSO_4.7H_2OFeCl_3{\cdot}6H_2O/FeSO_4{\cdot}7H_2O$ (Fe^{3+}:Fe^{2+}, 2:1 molar ratio) was added into chitosan solutions. After homogenization, 2 mL of NH_4OH was slowly added under US irradiation for 2 min (50% amplitude, in a pulse regime 20 s *on*–10 s *off*) using a G. Heinemann Ultraschall – und Labor techinik Sonifier. The resultant precipitated chitosan-based magnetite was removed from the solution by magnetic decantation. Then, obtained chitosan/Fe_3O_4 nanoparticles were washed several times with distilled water and redispersed in a glutaraldehyde (GL) solution (chitosan: GL, 2:1 molar ratio) at 50 °C for 2 h under mechanical stirring. The final product was washed several times with distilled water and dried in an oven at 50 °C for 48 h. The samples were collected as a black powder and labeled as ChM 0.1, ChM 0.05 and ChM 0.01, where the numbers 0.1, 0.05 and 0.01 correspond to the mass of chitosan used in the synthesis. The same strategy was used in the synthesis of “naked” Fe_3O_4 nanoparticles.

2.3. Characterization methods

X-ray Powder Diffraction (XRPD) analysis was performed to confirm the crystalline structures of magnetite present in chitosan/Fe_3O_4 nanocomposites. The samples were analyzed by X-ray powder diffractometer Xpert Pro MPD (Panalytical) using Bragg–Brentano geometry in the range of 15°–70° with a rate of $1^\circ\ min^{-1}$. CuKα radiation (k = 1.54059 Å) was used and the tube operated at 40 kV and 30 mA.

Fourier Transform Infrared Spectroscopy (FTIR) analysis was carried out in a PerkinElmer 2000 spectrophotometer used to record spectra in the range between 4000 and 400 cm^{-1}. Previously measurements, the samples were dried and grounded to powder and pressed (~10 mg of sample to 100 mg of KBr) in disk format.

The morphologic study was performed by Transmission Electron Microscopy (TEM). The images were recorded by using a JEOL JEM-1400 electron microscope operating at an accelerating voltage of 120 kV. The samples were prepared by diluting nanoparticles dispersion in distillated water. Then, one droplet of the sample was placed on 300 mesh carbon-coated cooper grids and dried overnight under ambient conditions. The size distribution was determined by measurement of 50 randomly selected particles in different regions of the expanding TEM image.

For thermogravimetric analysis (TG), 5 mg of nanoparticles were carried out in nitrogen atmosphere by employing a Thermogravimetric Analyzer Q50 V20. The loss of mass was monitored heating up samples from 25 to 900 °C in a rate of 10 °C min^{-1}. The zero time for the thermal degradation study was taken after temperature stabilization.

Magnetic properties were investigated by a Vibrating Sample Magnetometer (VSM) Mini 5 T from Cryogenic Ltd. Previously, the VSM was calibrated using a YIG sphere, and after measuring the mass of each sample, the magnetization was given in emu g^{-1}. The zero-field-cooled (ZFC) curve was obtained by cooling the samples (300–5 K) in the absence of an external field, upon reaching temperature an external field is applied and measured as a function of the increasing temperature. The field-cooled (FC) curve is obtained following the same ZFC procedure; instead, the samples are cooled in the presence of external field.

Cyclic voltammetry measurements were carried out with a potentiostatic (Autolab PGSTAT 101 Metrohn- Eco Chemie) controlled by a personal computer with Nova version 1.11.2 software using conventional three-electrode system. This is composed by a