



Synthesis route to δ -FeOOH nanodiscs



Tanja Jurkin^a, Goran Štefanić^b, Goran Dražić^c, Marijan Gotić^{b,*}

^a Ruder Bošković Institute, Division of Materials Chemistry, Laboratory for Radiation Chemistry and Dosimetry, Bijenička 54, Zagreb, Croatia

^b Ruder Bošković Institute, Division of Materials Physics, Laboratory for the Synthesis of New Materials, Bijenička 54, Zagreb, Croatia

^c National Institute of Chemistry, Hajdrihova 19, SI-1001 Ljubljana, Slovenia

ARTICLE INFO

Article history:

Received 10 December 2015

Received in revised form

13 February 2016

Accepted 4 March 2016

Available online 5 March 2016

Keywords:

Delta-FeOOH

Feroxyhyte

Nanoparticles

Dextran

Gamma-irradiation

Mössbauer

ABSTRACT

δ -FeOOH is a synthetic analogue of a relatively uncommon mineral feroxyhyte (δ' -FeOOH). The conventional syntheses of δ -FeOOH start from the Fe(II) salt and proceed by a rapid oxidation of iron(II) hydroxide with H_2O_2 . The new synthesis route to δ -FeOOH nanodiscs reported in this work is based on the γ -irradiation of a deoxygenated iron(III) chloride alkaline aqueous colloidal solution in the presence of 2-propanol and diethylaminoethyl-dextran hydrochloride (DEAE-dextran). γ -irradiation of the colloidal solution enabled the strong reducing conditions thus favouring the reduction of Fe(III) to Fe(II). Under such strong reducing conditions the white suspension characteristic of $Fe(OH)_2$ was formed. When the white suspension came into contact with oxygen from air it rapidly oxidized into stable green-gray suspension characteristic of Fe(II)-Fe(III) hydrochloride known as Green Rust I. In the conventional process of sample isolation the green-gray stable suspension transformed to δ -FeOOH reddish powder that consists of rather uniform regular nanodiscs. The synthesized δ -FeOOH nanodiscs are magnetic and contain a magnetically ordered component in the Mössbauer spectrum at room temperature. It is expected that the results of this work will have a strong impact on finding new synthetic routes to the δ -FeOOH.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

δ -FeOOH is a synthetic analogue of a relatively uncommon mineral feroxyhyte (δ' -FeOOH). δ -FeOOH possesses specific structural and magnetic properties and unlike all the other iron oxyhydroxide polymorphs it is magnetic at room temperature [1,2]. However, the magnetic properties of feroxyhyte depend critically on the crystallite and/or particle size [2]. Pollard and Pankhurst [3] have reported that the feroxyhyte (feroxyhite) behaviour is consistent with ferrimagnetism.

δ -FeOOH has been used in various applications [4–8]. For instance, Pereira et al. [5] have reported on the first use of nanostructured δ -FeOOH, with the band gap energy in the visible region, as a promising photocatalyst for the production of hydrogen from water. Pinto et al. [6] have used δ -FeOOH as a heterogeneous catalyst in order to stimulate the degradation of organic contaminants such as a cationic (methylene blue) and an anionic dye (indigo carmine). It has been shown that δ -FeOOH could activate H_2O_2 to produce reactive radicals, which then further promoted the degradation of the dyes. Chagas et al. [7] reported that δ -FeOOH released a controlled amount of heat if placed under AC magnetic field, which

δ -FeOOH classified as promising material for biomedical applications.

A typical synthesis of δ -FeOOH powder involves the precipitation of $Fe(OH)_2$ followed by rapid oxidation with H_2O_2 in an aqueous alkaline suspension. Gotić et al. [9] have reported that strong alkalinity of the mother liquor was an important factor for δ -FeOOH formation via the $Fe(OH)_2$ precursor. Besides, it has been found that a small amount of Fe^{3+} ions present in the $Fe(OH)_2$ precursor before the rapid oxidation of Fe^{2+} ions with H_2O_2 was not critical for the formation of δ -FeOOH as a single phase.

In this work, iron(III) precursor was γ -irradiated in the presence of DEAE-dextran, a robust amino-dextran polymer specially designed for biomedical applications and what is more important; it can fully stabilize (disperse) the nanoparticles in an early stage of formation thus forming colloidal solutions rather than suspensions. Quite surprisingly the γ -irradiation of the deoxygenated alkaline aqueous colloidal solution of iron(III) chloride in the presence of DEAE-dextran produced δ -FeOOH nanodiscs as an end product.

2. Materials and methods

2.1. Chemicals

All chemicals were of analytical purity and used as received. Milli-Q deionized water was used. Iron(III) chloride hexahydrate

* Correspondence to: Ruder Bošković Institute, Division of Materials Physics, Laboratory for the Synthesis of New Materials, Bijenička 54, 10000 Zagreb, Croatia.
E-mail address: gotic@irb.hr (M. Gotić).

($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), sodium hydroxide (NaOH) and 2-propanol ($(\text{CH}_3)_2\text{CHOH}$) were supplied by Kemika, Zagreb. Diethylaminoethyl (DEAE)-dextran hydrochloride (average molecular weight 500,000) was produced by Sigma.

2.2. Synthesis and characterization of δ -FeOOH Nanoparticles

0.0934 g (0.35 mmol) of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.3665 g of DEAE-dextran hydrochloride were dissolved in 20 mL of Milli-Q deionized water and then 0.308 mL of 2-propanol was added. The pH of thus prepared solution was adjusted to 9 by adding 2 M NaOH aqueous solution. The solutions were bubbled with nitrogen in order to remove the dissolved oxygen and then γ -irradiated (without stirring) in a closed glass vial using ^{60}Co source at the Ruđer Bošković Institute. The temperature upon γ -radiation did not exceed 25 °C (room temperature synthesis). The dose rate of γ -radiation was $\sim 7 \text{ kGy h}^{-1}$. The absorbed doses were 113 kGy (sample S1) and 429 kGy (sample S2). The samples were magnetic and they were isolated by decantation with the help of the magnet or by centrifugation followed by washing with ethanol. The isolated samples were dried under vacuum at room temperature and then characterized. The samples were characterized using Electron Microscopies, X-ray powder diffraction and Mössbauer spectroscopy (Section 1 in Supplementary data).

3. Results and discussion

Fig. 1 shows FE SEM images of powder samples S1 and S2 (additional SEM images are shown in Suppl. data). Sample S1 (Fig. 1a) consists of rather uniform thin disc-like (2D morphology) nanoparticles (NPs) having a diameter of about 250 nm (Fig. S0 in Suppl. data). Although the NPs are softly agglomerated, the discrete disc-like NPs are well-visible. The coarse surfaces of NPs suggest the hydrated surfaces of these disc-like NPs. Sample S2 (Fig. 1b) consists of highly stacked disc-like nanoparticles. Due to the high agglomeration some particles have pseudospherical shape. Taking together, the sample S2 consists of pseudospherical nanoparticles that are substructured from laterally aggregated disc-like nanoparticles.

Fig. 2 shows the TEM images and selected area electron diffraction (SAED) patterns of sample S1. Fig. 2a shows the disc-like NPs (nanodiscs) at low magnification. Some of the nanodiscs lie perpendicular to the view. Fig. 2b shows nanodiscs at higher magnification. Fig. 2c shows the high-resolution TEM image of the nanodisc's surface, whereas Fig. 2d shows the corresponding SAED patterns. The nanodisc surface (Fig. 2c) is heterogeneous and consists of small grains. One grain having a diameter of 4 nm is shown. SAED patterns reveal the presence of poorly crystalline α -FeOOH and δ -FeOOH (Fig. 2d and Section S3 in Suppl. data).

The XRD patterns of sample S1 and S2 (Fig. 3, panel A) revealed the presence of δ -FeOOH (feroxyhite, ICDD card No. 77-0247) as a dominant phase and α -FeOOH (goethite, ICDD card 29-0713) as a minor phase. Volume fractions of δ -FeOOH in the samples S1 and S2 were estimated from the results of quantitative crystal phase analysis (Section S3 in Suppl. data) at 0.71(2) and 0.73(2), respectively. Precise lattice parameters determination of δ -FeOOH in samples S1 and S2 (Section S3 in Suppl. data) indicates small increase of the δ -FeOOH lattice parameters in the sample S2. However, both values were close to the values given in the ICDD card 77-0247. The results of line broadening analysis (Section S3 in Suppl. data) indicate the significant size anisotropy in the sample S1 ($D_{100} \sim 31 \text{ nm}$ and $D_{101} \sim 12 \text{ nm}$), which is in line with its anisotropic disc-like morphology (Fig. 1a). In case of the sample S2, the volume averaged domain sizes calculated from the 100 and 101 lines of δ -FeOOH are very similar ($D_{100} \sim 16 \text{ nm}$ and

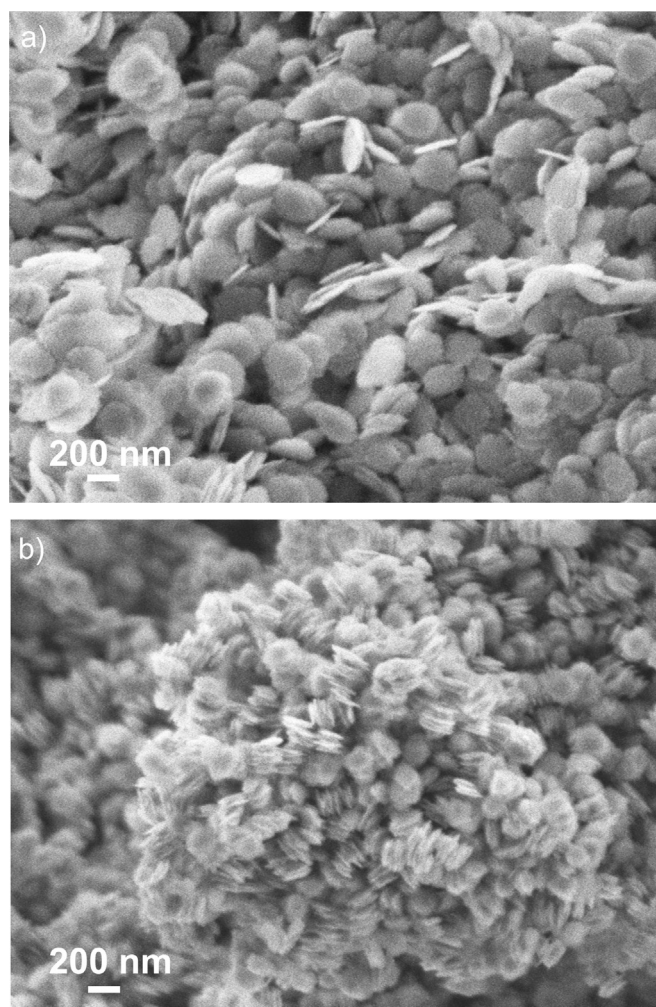


Fig. 1. SEM images of samples S1 (a) and S2 (b) that were γ -irradiated with dose of 113 and 429 kGy, respectively.

$D_{101} \sim 15 \text{ nm}$), which indicates the dominance of the 3D morphology in this sample. Diffraction lines of α -FeOOH appeared to be very broad, which indicate presence of ultrasmall nanoparticles estimated at $\sim 4.2 \text{ nm}$ and $\sim 5.1 \text{ nm}$ in samples S1 and S2, respectively (Section S3 in Suppl. data).

The room-temperature Mössbauer spectra of samples S1 and S2 (Fig. 3, panel B) are characterized with a collapsing sextet and a doublet. The collapsing sextet in Mössbauer spectrum can be assigned to FeOOH nanoparticles, whereas the doublet can be assigned to any paramagnetic/superparamagnetic particles [10–12] including α -FeOOH and/or δ -FeOOH. Since the XRD and TEM results confirmed that the sample S1 consisted of the well-crystallized δ -FeOOH having $\sim 29\%$ of poorly crystallized 4–5 nm- α -FeOOH (superparamagnetic range), the collapsing sextets in the Mössbauer spectra can arise from well-crystallized δ -FeOOH. The collapsing nature of sextets may be explained by stacking faults.

Fig. 4 shows the comparison of the conventional (a) and novel synthesis route to δ -FeOOH presented in this work (b). The conventional syntheses of δ -FeOOH start from iron (II) salt and continue by precipitation of $\text{Fe}(\text{OH})_2$ under inert atmosphere, which then rapidly oxidizes with H_2O_2 in an aqueous alkaline suspension. The new synthesis route to δ -FeOOH presented in this work started by dissolving iron(III)-chloride salt in DEAE-dextran hydrochloride aqueous solution at pH=9, the addition of 2-propanol and purging with nitrogen, which favoured the reducing conditions upon γ -irradiation [13–15]. Quite surprisingly the γ -

Download English Version:

<https://daneshyari.com/en/article/8017066>

Download Persian Version:

<https://daneshyari.com/article/8017066>

[Daneshyari.com](https://daneshyari.com)