Synthesis and properties of nanostructured Cr-doped hematite fibres

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Abstract

Cr-doped α-Fe_2O_3 fibres were synthesized by combining electrospinning and the thermal treatment of electrospun composite fibres at 500°C. XRD analysis showed the formation of solid solutions with a corresponding small decrease in the unit-cell volume due to a difference between the ionic radii of Fe^{3+} and Cr^{3+} cations. Mössbauer spectroscopy showed that the incorporation of Cr^{3+} into the α-Fe_2O_3 crystal structure induced a decrease in the hyperfine magnetic field. Doping of α-Fe_2O_3 with Cr^{3+} also influenced the shape and position of IR bands in relation to reference α-Fe_2O_3 fibres in the corresponding FT-IR spectra. The FE-SEM images of Cr-doped α-Fe_2O_3 fibres showed that they consisted of interconnected nanoparticles and possessed a hollow substructure. The photocatalytic degradation of rhodamine B using electrospun fibres was also investigated.

Keywords: α-Fe_2O_3; Cr-doping; electrospinning; XRD; FE-SEM; spectroscopy; photocatalysis

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Introduction

Over the last decade investigations related to hematite (α-Fe_2O_3) doping with different metal cations have been intensified. These investigations were mainly motivated by their potential for various applications. Generally, it is known that doping with metal cations may enhance a specific property of hematite, thus enabling a corresponding application of that material. Among many metal cations chromium cation (Cr^{3+}) is a convenient dopant owing to very similar ionic radii of Fe^{3+} (64.5 pm) and Cr^{3+} (61.5 pm) and because hematite and eskolaite (Cr_2O_3) are isostructural with corundum (α-Al_2O_3).

Cr-doped hematites with an enhanced photoelectrochemical (PEC) activity were investigated (Kleiman-Shwarsctein et al. 2008; Shen et al. 2012; Bouhjar et al. 2018) for a possible use as photoanode in water splitting. Liu et al. (2019) prepared Cr-doped hematite using ball-milling combined with the heat treatment of the resulting mixture. The authors showed that 4 at. % Cr-doped hematite as electrode material significantly enhanced the reversibility capacity relative to undoped hematite in Li-ion batteries. It was also shown that Cr-doped hematite nanoparticles can be utilized as a highly selective and sensitive H_2S sensor at low temperatures (Xue et al. 2019). Oćwieja et al. (2017) tested Cr-doped hematite nanoparticles as a catalyst in the high temperature water gas shift (HT-WGS) reaction.

The properties of hematite doped with various metal cations depend both on the nature of the metal dopant and the synthesis method. Also, the morphology and size of doped hematite in the form of particles, fibres or films influence the material properties. In the present work we report new results about doping of α-Fe_2O_3 with Cr^{3+} cations. The conditions for the synthesis of Cr-doped α-Fe_2O_3 fibres by combining electrospinning and the thermal treatment of composite electrospun fibres as well as the properties of thus prepared samples were examined. Electrospinning is a unique experimental method in the preparation of various nanofibers, many of which already found applications in ceramics, organic polymers, engineering, biomedicine, etc. (Ramakrishna et al. 2005).

Experimental

Preparation of samples

Polyvinylpyrrolidone (PVP; M_w=1 300 000), $Fe(NO_3)_3 \cdot 9H_2O$ and $Cr(NO_3)_3 \cdot 9H_2O$ were supplied by *Alpha Aesar*, absolute ethanol by *Gram-mol* (Zagreb, Croatia), concentrated acetic acid (99,5%) by *Alkaloid* (Skopje, North Macedonia) and miliQ water were used. In the photocatalytic experiment 30 % wt. H_2O_2 by *Kemika* (Zagreb, Croatia) and rhodamine B (RhB) by *Merck* were supplied. Commercial hematite powder was supplied by Ventron Chemicals Ltd.

A viscous solution was prepared by dissolving 3g PVP into 50 mL C_2H_5OH, continued by mixing at 350 rpm and 70°C for 3h. Into 20 mL of thus prepared viscous solution 2 ml of H_2O and 20 drops of concentrated acetic acid were added and subsequently mixed at 350 rpm and RT for 1h. Then the appropriate volumes of 1M $Fe(NO_3)_3\cdot 9H_2O$ and $Cr(NO_3)_3\cdot 9H_2O$ were added to obtain 5 and 10 mol % Cr-doped hematite samples at the end of the experiment. Upon homogenization (3h mixing) of this viscous solution the electrospinning experiment started. In order to obtain reference samples α-Fe_2O_3 and Cr_2O_3 viscous solutions containing only $Fe(NO_3)_3$ or $Cr(NO_3)_3$ were also prepared.

The electrospinning device was set up using the Harvard Apparatus (Pump11 Elite) and high-voltage auto-reserving power supply CZE1000R manufactured by *Spellman* (N.Y., USA). The metallic nozzle was connected to the positive terminal of the power supply source and voltage was adjusted to 20 kV. The negative end was grounded and connected to the aluminium plate sized 15 cm × 20 cm. This aluminium plate was covered with thick aluminium foil (0.030 mm) for collecting the electrospun material. The distance between the metallic nozzle tip (needle 21G) and the aluminium plate was 20 cm. Thus prepared electrospun fibres on aluminium foil were put in vacuum for at least 15h at RT. Fibre mats were then heated in the laboratory oven in ceramic crucibles without the aluminium foil. Temperature in the oven was gradually increased by 10°C/min up to 500°C and after 3h heating the samples were left to cool slowly to RT inside the furnace. It should be noted that every sample was also prepared in the form of thin fibre mats on aluminium foil, obtained by only 10 minutes of electrospinning. The mentioned thin fibre mats (1-2 cm^2 in surface) were calcined with aluminium foil in ceramic crucibles.

Instrumentation

XRD patterns were recorded with a Panalytical Aeris powder diffractometer using $CuK\alpha_{1,2}$ radiation. In the evaluation of XRD patterns the programs Match! and Dicvol06 were used.

Mössbauer spectra were recorded using a spectrometer set up with modules by *Wissenschaftliche Elektronik GmbH.* A Mössbauer source ^{57}Co in the rhodium matrix was used, The Mössbauer spectrometer was calibrated with α-Fe. The MossWinn computer program was used to evaluate the recorded spectra.

FT-IR spectra were recorded using a Frontier spectrometer manufactured by *Perkin Elmer*.

UV-Vis spectra were recorded with a Shimadzu 3600 spectrometer linked to an integrating sphere. The samples were put on top of $BaSO_4$ powder (*WAKO Chemicals*), spread on its surface and then pressed into a holder.

The electrospun Cr-doped α-Fe_2O_3 fibres were also characterized with an FE-SEM model JSM-7000F manufactured by *JEOL* linked to the EDS/INCA 450 (energy dispersive X-ray analyzer) manufactured by *Oxford Instruments*. The fractions of iron and chromium in the samples were confirmed by EDS measurements.

The photocatalytic measurements were conducted with a MAX-303-Compact Xenon Light source with 300W lamps manufactured by *Asahi Spectra*. The apparatus was supplied with suitable filters. The procedure for the photocatalytic measurement was as follows: the suspension containing 10 mg of photocatalyst and having 0.02 mM RhB in 50 mL miliQ water was mixed at 300 rpm for 1h in darkness. 255 μL of 30 wt % H_2O_2 was added to thus prepared suspension and subsequently mixed for the next 30 min in darkness. After that the clear solution was separated from the solid photocatalyst by centrifugation at 5000 rpm for 5 min and the UV/Vis spectrum was recorded to obtain the first point on the time scale. The other points were obtained by illuminating the suspension by visible light ($420 \text{ nm} < \lambda < 600 \text{ nm}$) up to 3h. The light source was at a 10 cm distance from the surface. After each illumination and UV/Vis spectrum measurement the clear solution and sediment were returned into the original suspension to keep the starting concentration conditions. The photocatalytic degradation of RhB was followed by the ratio of the maximum absorbance of the measured aliquot and the maximum absorbance of the initial sample.

Results and discussion

Fig. 1 shows the FE SEM images of electrospun α-Fe_2O_3, Cr-doped α-Fe_2O_3 and Cr_2O_3 fibres (samples Cr0 (no chromium), Cr5 (5 mol % Cr), Cr10 (10 mol % Cr) and Cr100 (no iron)). These images confirm that adequate chemical and physical conditions were provided for the fibres formation. At higher magnification the FE SEM images (Fig. 2) of Cr-doped hematite samples Cr5 (a,b) and Cr10 (c,d) showed that the fibres consist of interconnected nanoparticles. The hollow substructure of grinded Cr5 fibres was visible. The formation of nanocoils was observed in Cr10 fibres. As in the case of Cr5 fibres the hollow substructure was also present in Cr10 fibres. The diameter of the nanoholes in Cr5 and Cr10 fibres varied. The average diameters of electrospun fibres were determined: 85 nm for Cr0, 102 nm for Cr5, 142 nm for Cr10 and 101 nm for Cr100. The pores diameter varied between 36 and 46 nm.

Fig. 3 shows the XRD patterns of samples Cr0 to Cr100, and the calculated crystallographic parameters are given in Table 1. The XRD patterns of samples Cr0 and Cr100 correspond to hematite (α-Fe_2O_3) and eskolaite (Cr_2O_3), respectively. Table 1 shows a decrease in the unit-cell volume in the order Cr0 to Cr100. The incorporation of Cr^{3+} into the α-Fe_2O_3 crystal structure decreased the unit-cell volume, which can be related to a smaller ionic radius of Cr^{3+} than that of Fe^{3+}. Table 1 also shows that the incorporation of Cr^{3+} into the α-Fe_2O_3 crystal structure induced an increased crystallite size as calculated using the Scherrer equation.

Fig. 4a shows the RT Mössbauer spectra of samples Cr0, Cr5 and Cr10, with calculated Mössbauer parameters given in Table 2. A gradual decrease in the hyperfine magnetic field B_{hf} with the increased amount of Cr-dopant was noticed. The distribution of hyperfine magnetic fields showed a broadening effect brought about by the incorporation of Cr^{3+} into the α-Fe_2O_3 crystal structure (Fig. 4b). Generally, the formation of solid solutions in the system $(Fe_{1-x}Cr_x)_2O_3$ and their properties are dependent on the preparation procedure (Musić et al. 1993; Tsokov et al. 1993; Musić et al. 1996; Grygar et al. 2003). Berry et al. (2000) synthesized α-Fe_2O_3 doped with 10% of Sn^{4+}, Ti^{4+} or Mg^{2+} by the hydrothermal procedure. Neutron powder diffraction showed that the dopant cations occupy both interstitial and substitutional sites in α-Fe_2O_3. RT Mössbauer spectra were evaluated using the superposition of two sextets. Moreover, the Neel temperatures of Sn- and Mg-doped α-Fe_2O_3 were lower in relation to pure α-Fe_2O_3.

Fig. 5 shows the FT-IR spectra of samples Cr0 to Cr100 as well as the commercial α-Fe_2O_3. The IR bands recorded for sample Cr0 can be assigned to α-Fe_2O_3 as a single phase. Generally, the FT-IR spectrum of α-Fe_2O_3 shows six active vibrations, two A_{2u} ($E \parallel c$) and four E_u ($E \perp c$). The parameters (ω_T and ω_L) of a harmonic oscillator model applied to α-Fe_2O_3 are given in reference literature (Onari et al. 1977; Serna et al. 1987; Wang et al. 1998). These works showed that the shape of the corresponding FT-IR spectrum and the positions of IR bands were depending on the shape and size of α-Fe_2O_3 particles. Fig. 5 shows that doping α-Fe_2O_3 with Cr^{3+} cations also influenced the corresponding FT-IR spectra. In the direction Cr0 to Cr10 the following shifts of IR bands were noticed: 384 to 392 cm^{-1}, 436 to 441 cm^{-1}, 519 to 524 cm^{-1} and 649 to 654 cm^{-1}.

Samples Cr5 and Cr10 showed the formation of pronounced shoulders at 474/475 cm^{-1} as a direct consequence of Cr-doping. The FT-IR spectrum of sample Cr100 can be assigned to Cr_2O_3 as a single phase. Serna et al. (1982) reported about the impact of the shape and size of Cr_2O_3 particles on the corresponding IR spectrum as in the case of other corundum-type oxides. IR measurements on single-crystal Cr_2O_3 showed that the vibration modes parallel to the c-axis were positioned at 538 and 613 cm^{-1}, whereas the vibration modes perpendicular to the c-axis were positioned at 417, 444, 532 and 613 cm^{-1} (Renneke and Lynch 1965). The capabilities of infrared spectroscopy in the detection of adsorbate-adsorbent and adsorbate-adsorbate interactions between CO and Cr_2O_3 (Scarano and Zecchina 1987) and the formation of Cr_2O_3 in the films during the oxidation of Inconel 718 alloy were documented (Lenglet et al. 1990).

Fig. 6 shows UV/Vis/NIR spectra recorded for samples Cr0 to Cr100 and the direct band gaps determined by the Tauc plot. The electrospun α-Fe_2O_3 fibres (sample Cr0) are characterized with the bands at 352, 478, 668 and 862 nm. A small relative intensity band at~304 nm was noticed for samples Cr5 and Cr10. The origin of the UV/Vis spectrum of α-Fe_2O_3 is discussed in reference literature (Kleiman-Shwarsctein et al. 2008; Ristić et al. 2018). In Fig. 6 the direct band gaps are also shown for samples Cr0 to Cr100, as calculated using the Tauc plot method. In Fig. 7 the linear parts of the curves are shown in shadow and the corresponding plots are intersected with the x-axis to obtain a direct band gap (E_g/eV). The direct band gap decreased from 2.15 to 2.03 in the series for samples Cr0 to Cr10, whereas the direct band gap for sample Cr100 was measured at 3.06 eV.

The photocatalytic activities of samples Cr0 to Cr100 as well as the commercial α-Fe_2O_3 were tested using rhodamine B (RhB) degradation under visible light. The results are summarized in Fig. 8 and Table 3. It was noticed that sample Cr0 showed the highest photocatalytic degradation of RhB under given conditions (92% and 17% without illumination) which is higher than in the case of commercial α-Fe_2O_3 (52%). Fig. 9 illustrates with the corresponding UV/Vis spectra the photocatalytic degradation of RhB in sample Cr0 (a = no illumination, b = illumination).

It can be assumed that the effects noticed during degradation of RhB are due to combine catalytic (in dark) and photocatalytic (with illumination) activities of Cr5 to Cr100 samples. In Cr-doped hematites in the presence of hydrogen peroxide it is possible the catalytic oxidation of Cr(III) to Cr(VI) at the hematite surface probably forming Cr(VI)-oxide. Generally, it is known that mixed iron(III)/chromium(III) oxides are good catalysts. In this sense Cr(III)-dopant differs from other metal dopants, for example Zn(II) in hematite (Kumar et al. 2019).

Earlier authors reported that some properties (see Introduction (Kleiman-Shwarsctein et al. 2008; Shen et al. 2012; Bouhjar et al. 2018; Liu et al. 2019; Xue et al. 2019)) of Cr-doped α-Fe_2O_3 were enhanced relative to undoped α-Fe_2O_3 and for this reason would be good in the future to test the electrospun Cr-doped fibres in these applications. To the best of our knowledge, the data about such applications using electrospun Cr-doped α-Fe_2O_3 fibres are not available in reference literature. Zhou et al. (2012) investigated the photodegradation of rhodamine B in the presence of H_2O_2 by visible light in dependence on different α-Fe_2O_3 architectures (1D nanorods, 2D nanoplates and 3D nanocubes). These authors found an order of photo-efficiency for different crystallographic planes $\{110\}>\{012\},\{001\}$.

Conclusions

The formation of Cr-doped α-Fe_2O_3 fibres by utilizing the method of electrospinning was investigated. Reference electrospun α-Fe_2O_3 and Cr_2O_3 fibres were also prepared. The XRD analysis of Cr-doped α-Fe_2O_3 samples showed only the presence of one phase corresponding to the α-Fe_2O_3 crystal structure. The incorporation of Cr^{3+} ions into the α-Fe_2O_3 crystal structure slightly decreased the unit-cell volume, which can be related to Cr^{3+} ionic radius being smaller than that of Fe^{3+} ions, and on the other hand the crystallite size increased. The incorporation of Cr^{3+} ions also decreased the hyperfine magnetic field as shown by the Mössbauer spectroscopy. The FE-SEM images showed that Cr-doped α-Fe_2O_3 fibres consisted of interconnected nanoparticles. The hollow substructure of Cr-doped α-Fe_2O_3 fibres was found. A certain effect of Cr-doping on the shape and positions of IR bands in the FT-IR spectra was noticed. The photocatalytic degradation of rhodamine B with reference α-Fe_2O_3 fibres and Cr-doped α-Fe_2O_3 fibres was also documented.

Conflict of Interest Statement

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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Table 1

Unit cell parameters of the samples.

Sample	a / Å	c / Å	V / Å^3	Crystallite size* / Å
Cr0	5.0355(8)	13.753(2)	302.02	453
Cr5	5.0355(9)	13.745(3)	301.85	503
Cr10	5.0321(6)	13.729(2)	301.09	613
Cr100	4.9560(6)	13.586(3)	289	327

*Crystallite sizes were estimated by Scherrer equation.

Table 2

^{57}Fe Mossbauer parameters obtained for samples Cr0, Cr5 and Cr10.

Sample	Line	δ / mm s^{-1}	Δ or E_q /mm s^{-1}	B_{hf} / T	Γ / mm s^{-1}	Area /%
Cr0	M	0.36	-0.20	51.0	0.23	100
Cr5	M	0.37	-0.21	50.9	0.26	100
Cr10	M	0.37	-0.22	50.6	0.27	100

Key: δ=isomeric shift relative to α-Fe at RT, B_{hf}= hyperfine magnetic field, Δ or E_q=quadrupole splitting, Γ=line-width, M=sextet, Q=quadrupole doublet

Errors: δ and E_q or $\Delta = \pm 0.01$ mm s^{-1}, $B_{hf} = \pm 0.2$ T

Remark: Mössbauer spectra were fitted using the distribution of hyperfine magnetic fields.

Table 3

Photocatalytic efficiency of RhB degradation.

Sample	RhB degradation after 3h of illumination	
Commercial α-Fe_2O_3	52%	
Cr0	92%	(17% without illumination)
Cr5	86%	
Cr10	57%	
Cr100	73%	(68% without illumination)

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Figure captions

Fig. 1 FE SEM images of samples Cr0 (no chromium), Cr5 (5 mol % Cr), Cr10 (10 mol % Cr) and Cr100 (no iron).

Fig. 2 FE SEM images at higher magnification of samples Cr5 (a,b) and Cr10 (c,d).

Fig. 3 XRD patterns of samples Cr0 to Cr100. Reference XRD pattern of hematite (α-Fe_2O_3) and eskolaite (Cr_2O_3) are also shown.

Fig. 4 (a) RT Mössbauer spectra of samples Cr0, Cr5 and Cr10, (b) the corresponding hyperfine magnetic field (B_{hf}) distributions.

Fig. 5 FT-IR spectra of samples Cr0, Cr5, Cr10, Cr100 and commercial α-Fe_2O_3 are shown.

Fig. 6 UV/Vis/NIR spectra of samples Cr0 to Cr100; Direct band gap values are shown for these samples; At the top-right corner of each spectrum are the photos showing true colour of prepared samples.

Fig. 7 Tauc plot method was used to calculate direct band gaps for samples Cr0 to Cr100; The linear parts in curves are shown in shadow and the corresponding plots are intersected with x-axis to obtain the direct band gaps (E_g / eV).

Fig. 8 Photocatalytic efficiency in decomposition of rhodamine B (c/c_0 vs. time of illumination) as determined for samples Cr0 to Cr100 and commercial α-Fe_2O_3.

Fig. 9 Photocatalytic decomposition of rhodamine B with sample Cr0 as shown by the changes in visible part of the optical spectrum ((a) without illumination, (b) with illumination).