

PREPARATION AND PROPERTIES OF ELECTROSPUN Cr-DOPED α -Fe₂O₃ NANOFIBERS

Marko Robić¹, Mira Ristić¹, Željka Petrović¹, Marijan Marciuš¹, Stjepko Krehula¹ and Svetozar Musić^{1,2}

1 - Division of Materials Chemistry, Ruđer Bošković Institute, P.O. Box 180, HR-10002 Zagreb, Croatia

2 - Croatian Academy of Science and Arts, Zrinski trg 11, HR-10000 Zagreb, Croatia

Marko.Robic@irb.hr

Introduction

Hematite (α -Fe₂O₃) is the most stable and the most common iron oxide phase [1]. Due to high stability in aqueous solutions, low toxicity, abundance and low cost, it has been extensively investigated for possible applications. Hematite strongly absorbs UV and visible light with energies above its band gap of 2.2 eV. For this reason, it has been investigated as a photoelectrode for photoelectrochemical water splitting [2] and as a photocatalyst for decomposition of organic pollutants [3]. The performance of hematite in these applications can be improved by using nanostructured hematite samples doped with different metal cations [2,3].

Electrospinning is an excellent method to produce nanostructured hematite fibers possessing a high specific surface area [4,5]. This property is essential in many applications (catalysts, photocatalysts, photoelectrodes, battery electrodes, supercapacitors, adsorbents, etc). Due to the same charge and similar effective ionic radius of Fe³⁺ and Cr³⁺ ions (64.5 and 61.5 pm, respectively), solid solutions α -(Fe_{1-x}Cr_x)₂O₃ can be prepared in the whole Fe-Cr concentration range ($0 \leq x \leq 1$) [6,7] with a gradual reduction of unit cell as Cr content increases. Optical spectra of Cr-doped hematite showed a reduction of the direct and indirect optical band gap to lower energies compared to pure hematite [7,8].

Aim of the present work was to prepare hematite nanofibers, Cr-doped hematite nanofibers and eskolaite (α -Cr₂O₃) nanofibers using electrospinning method and to investigate their structural, optical and photocatalytic properties.

Experimental

Viscous solutions containing dissolved polyvinylpyrrolidone PVP ($M_w = 1\,300\,000$ g/mol), acetic acid, water and nitrate salts (Fe³⁺, Cr³⁺) in ethanol were electrospun, dried in vacuum and calcined (for 3h at 500°C) to obtain desired metal oxide nanofibers. Electrospinning was carried out on 20 kV, flow rate was 1.5 mL/h and distance from needle tip to collector was 20 cm. Thus obtained fibers were characterized by several methods (UV-Vis-NIR, FE-SEM & EDS, Mössbauer, FTIR (ATR), TG-DTA, XRPD). A reduction of the direct and indirect optical band gap by Cr doping was estimated using Tauc plots. Visible light photocatalytic activities of the prepared samples were tested by decomposition of rhodamine B dye in the presence of H₂O₂ under visible light illumination.

Results

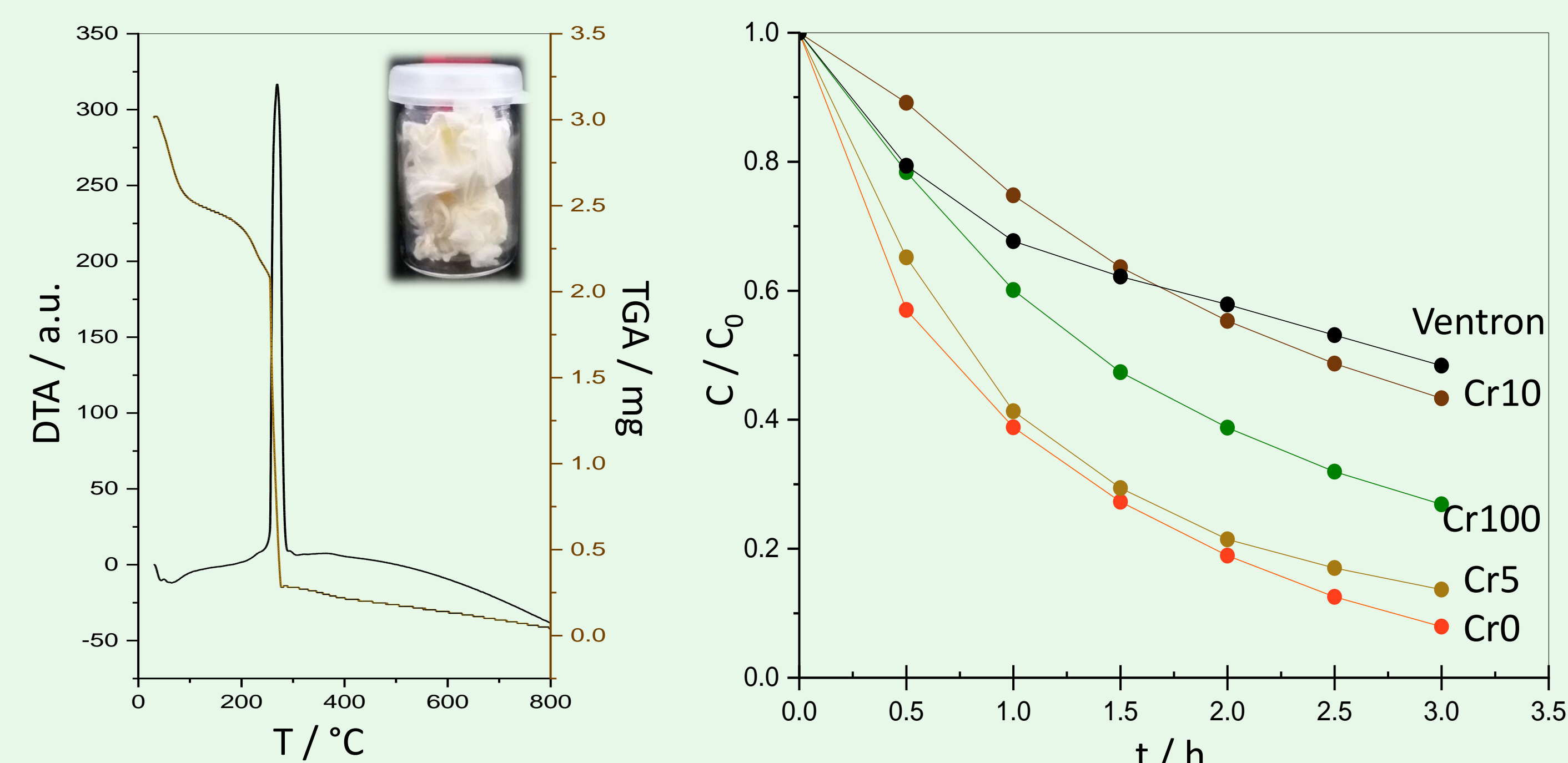
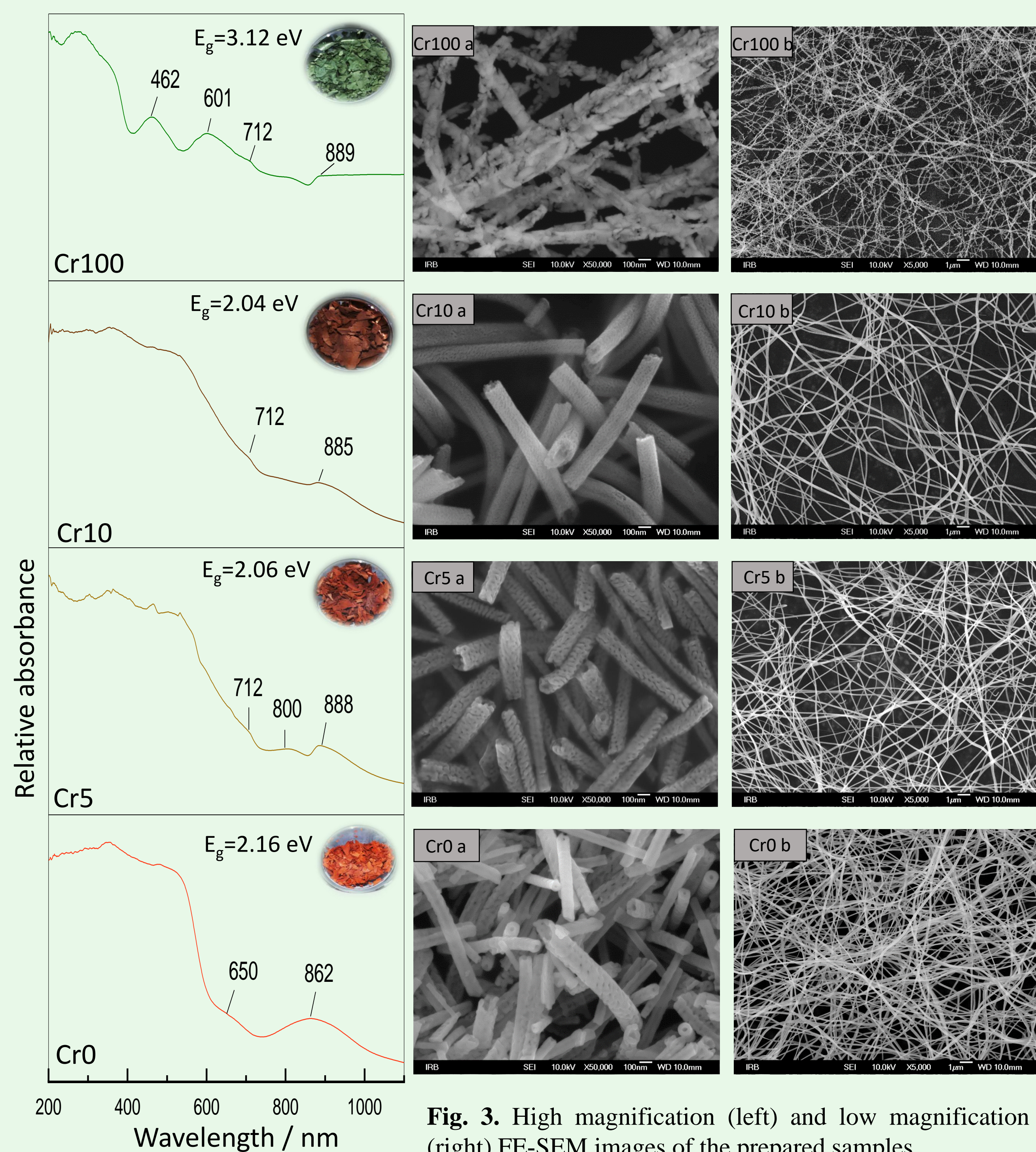


Fig. 7. The photocatalytic efficiency of examined samples and commercial α -Fe₂O₃ by Ventron.

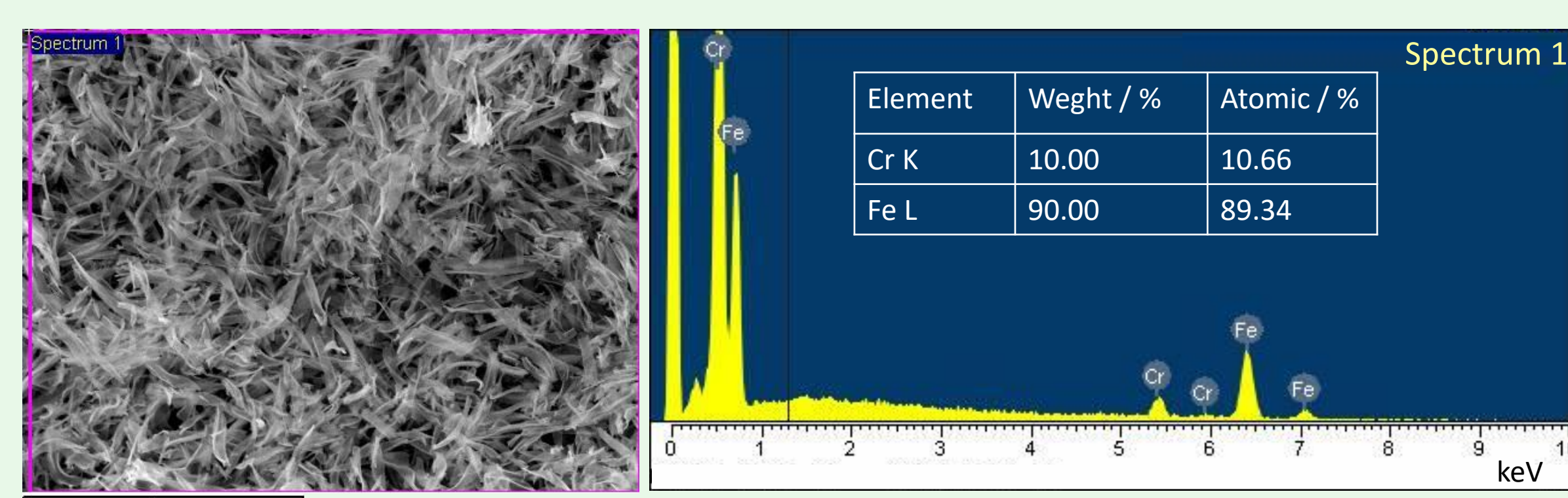


Fig. 1. EDS analysis of sample Cr10 with associated FE-SEM image.

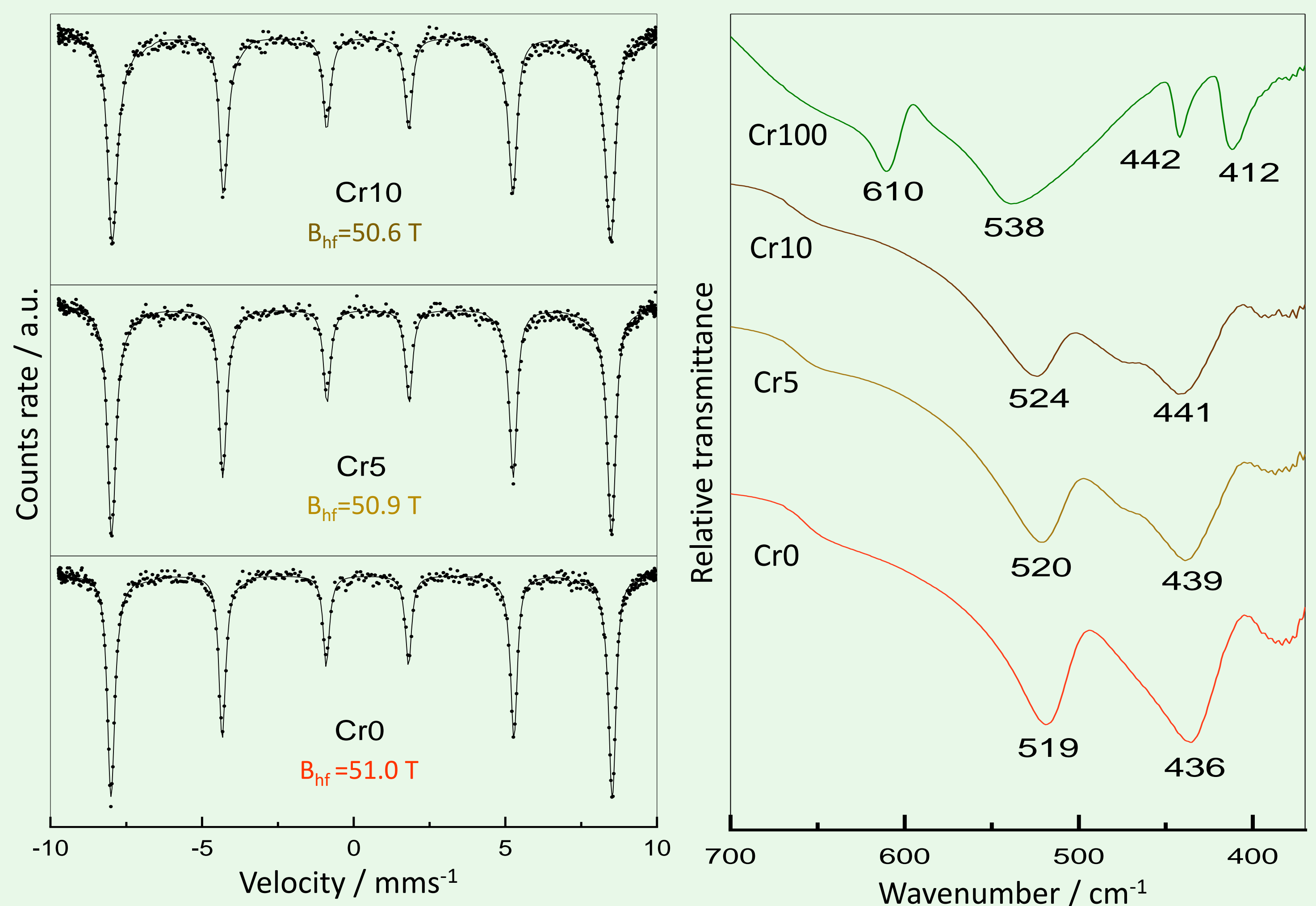


Fig. 4. ⁵⁷Fe Mössbauer spectra recorded at RT. Spectra were fitted using the distributions of hyperfine magnetic field.

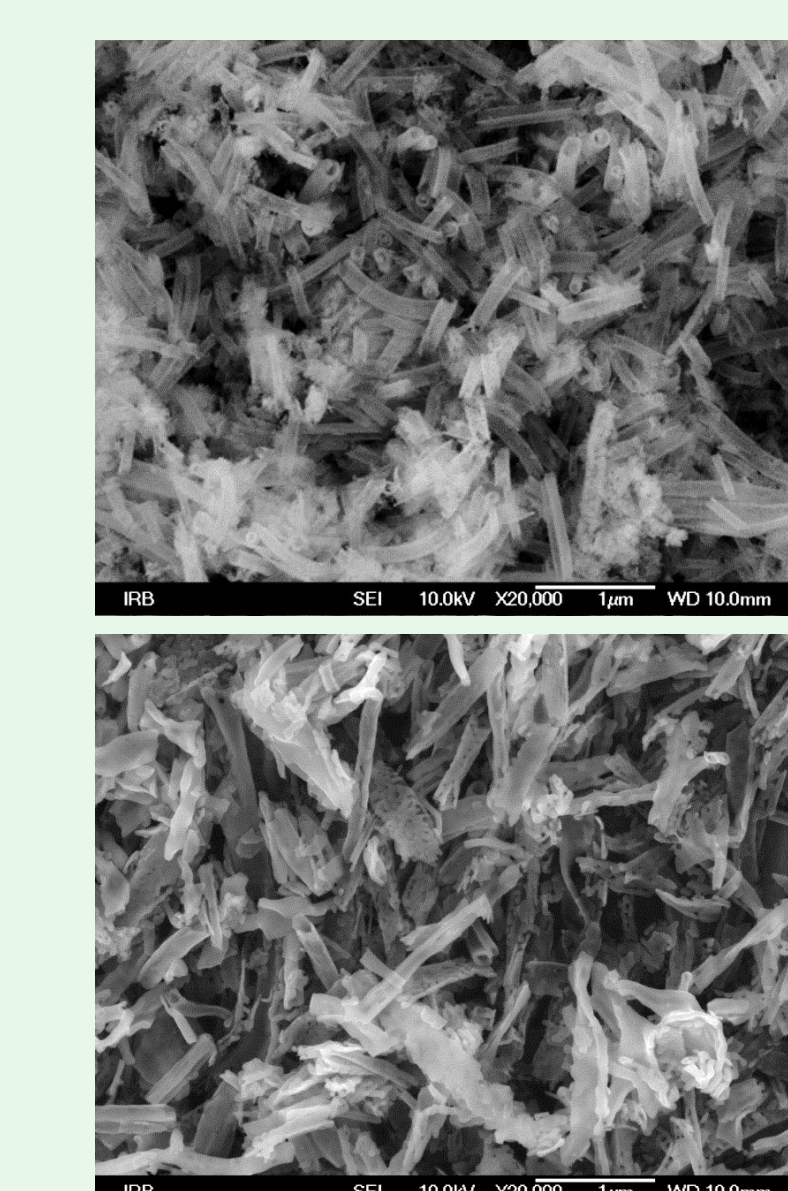
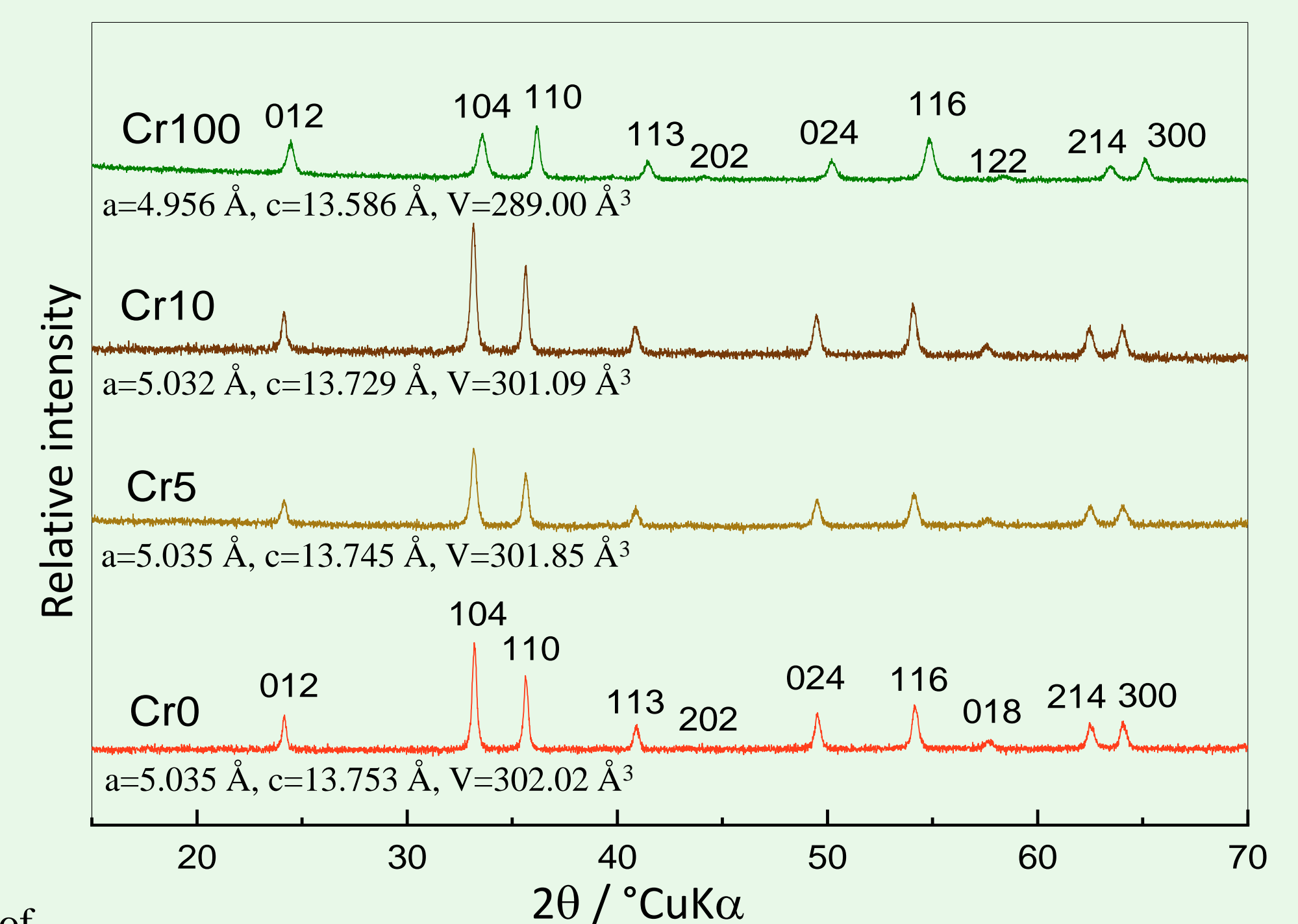


Fig. 8. FE-SEM images of samples Cr0 (bottom) and Cr100 (top) after photocatalysis.



Conclusions

- Electrospinning method (single needle) was used to successfully obtain hollow Cr₂O₃ and α -Fe₂O₃ nanofibers, as well as Cr-doped hematite nanofibers.
- Doping with chromium caused many changes: increased fiber diameter, decreased unit cell volume, decreased hyperfine magnetic field, decreased optical band gap and decreased photocatalytic activity. FTIR peaks shifted to higher wavenumbers. Doping also caused the color change of prepared samples from orange-red (Cr0) to brown (Cr10).
- Cr₂O₃ nanofibers showed catalytic activity, but they were not photo-active.

Acknowledgement:

This work is financially supported by Croatian Science Foundation (HRZZ), project number, IP-2016-06-8254.

References:

- R.M. Cornell, U. Schwertmann, The Iron Oxides, Structure, Properties, Reactions, Occurrence and Uses, second ed., Wiley-VCH, Weinheim, 2003.
- K. Sivula, F. Le Formal, M. Grätzel, ChemSusChem 4 (2011) 432–449.
- M. Mishra, D.-M. Chun, Appl. Catal. A: Gen. 498 (2015) 126–141.
- C.T. Cherian et al., J. Mater. Chem. 22 (2012) 12198–12204.
- G. Binitha et al. J. Mater. Chem. A 1 (2013) 11698–11704.
- T. Grygar, P. Bezdička, J. Dědeček, E. Petrovsky, O. Schneeweiss, Ceram.-Silikaty 47 (2003) 32–39.
- H. Mashiko, T. Oshima, A. Ohtomo, Appl. Phys. Lett. 99 (2011) 241904.
- S.E Chamberlin et al., J. Phys.: Condens. Matter 25 (2013) 392002.