ELECTROSPUN Ti−DOPED HEMATITE FIBRES AND THEIR PROPERTIES

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Introduction

In the last few decades, a significant number of investigations appeared with the aim to find the best materials for photoelectrochemical (PEC) water splitting or photocatalytic decontamination of polluted water. Hematite (α-Fe_2O_3) was selected as a potential material for these applications because it has a suitable band gap value (~2.1 to 2.2 eV) and can absorb a large portion of the visible solar spectrum. It is well-known that hematite properties can be improved by doping with various cations. For example, Ti-doped α-Fe_2O_3 was often investigated as a promising photoanode in photoelectrochemical water splitting. For mentioned applications Ti-doped α-Fe_2O_3 samples were commonly prepared in the form of films using methods like the atmospheric pressure chemical vapour deposition [1], pulsed laser deposition [2], electrospraying [3] or electrospinning [4]. Electrospinning is a unique method in the synthesis of various nanofibres which found application in science, engineering and biomedicine [5].

In the present research we report the formation of Ti-doped α-Fe_2O_3 (Ti5 and Ti10), α-Fe_2O_3 (Ti0) and TiO_2 (Ti100) fibres using electrospinning as the synthesis method. All samples were characterized with FE SEM, XRPD, ^{57}Fe Mössbauer, FT-IR and UV/Vis/NIR. Photocatalytic activity of prepared samples was also tested.

Experimental

Cation salts: $Fe(NO_3)_3 \cdot 9H_2O$ and Ti(IV)-isopropoxide
Solvent: ethanol
pH adjustment: glacial acetic acid
Polymer: PVP (1 300 000 M)

Electrospinning solution
cation salts solutions were slowly added to the viscous solution, 3h of stirring

→ **Electrospinning**
tip to collector distance: 10 cm
flow rate: 25µL/min
voltage: 20 kV

→ **Drying**
vacuum dryer
RT, >15h

→ **Calcination**
3h, 550°C, 10°C/min

Results

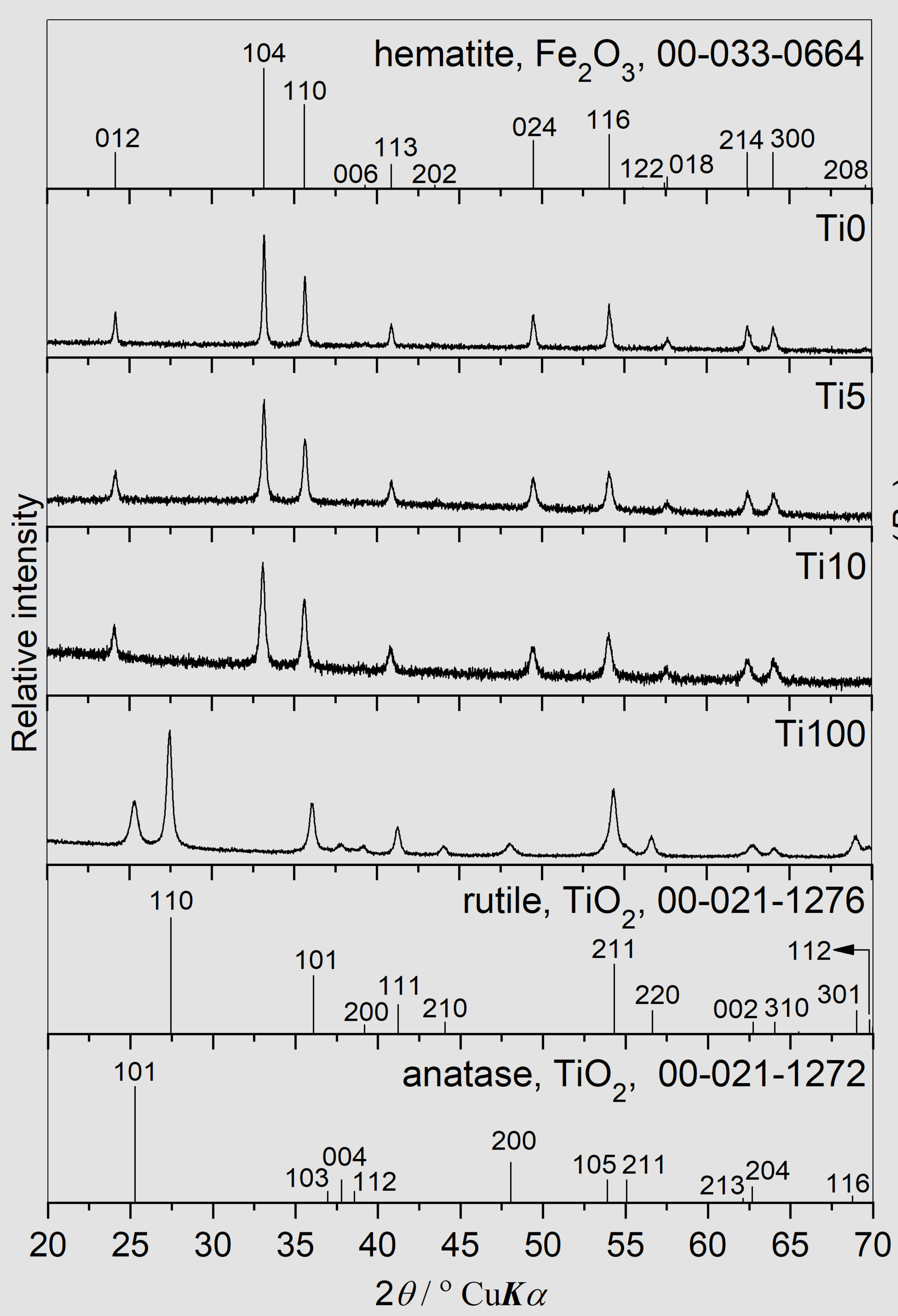


Fig. 1. XRPD patterns of prepared samples.

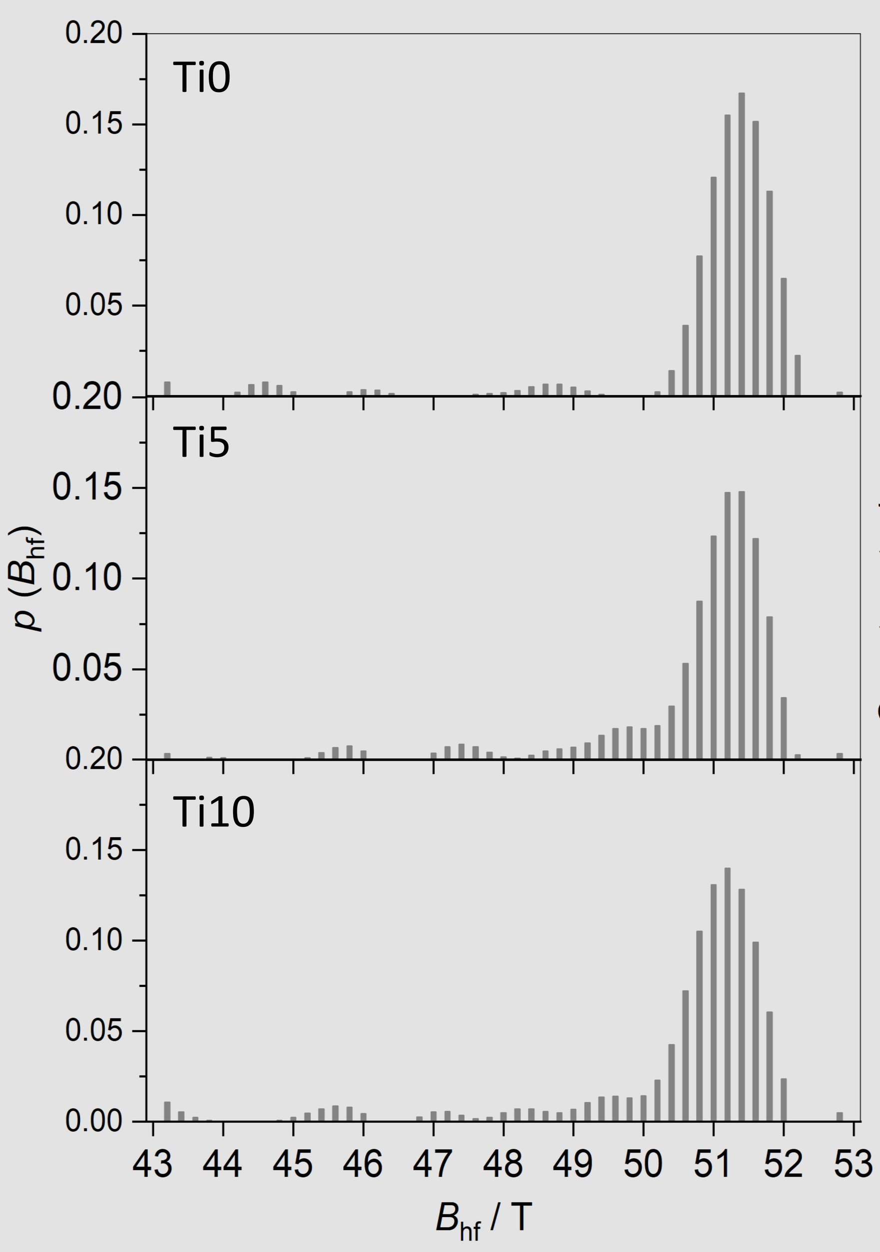


Fig. 2. HMF distributions of prepared hematite and Ti-doped hematite fibres.

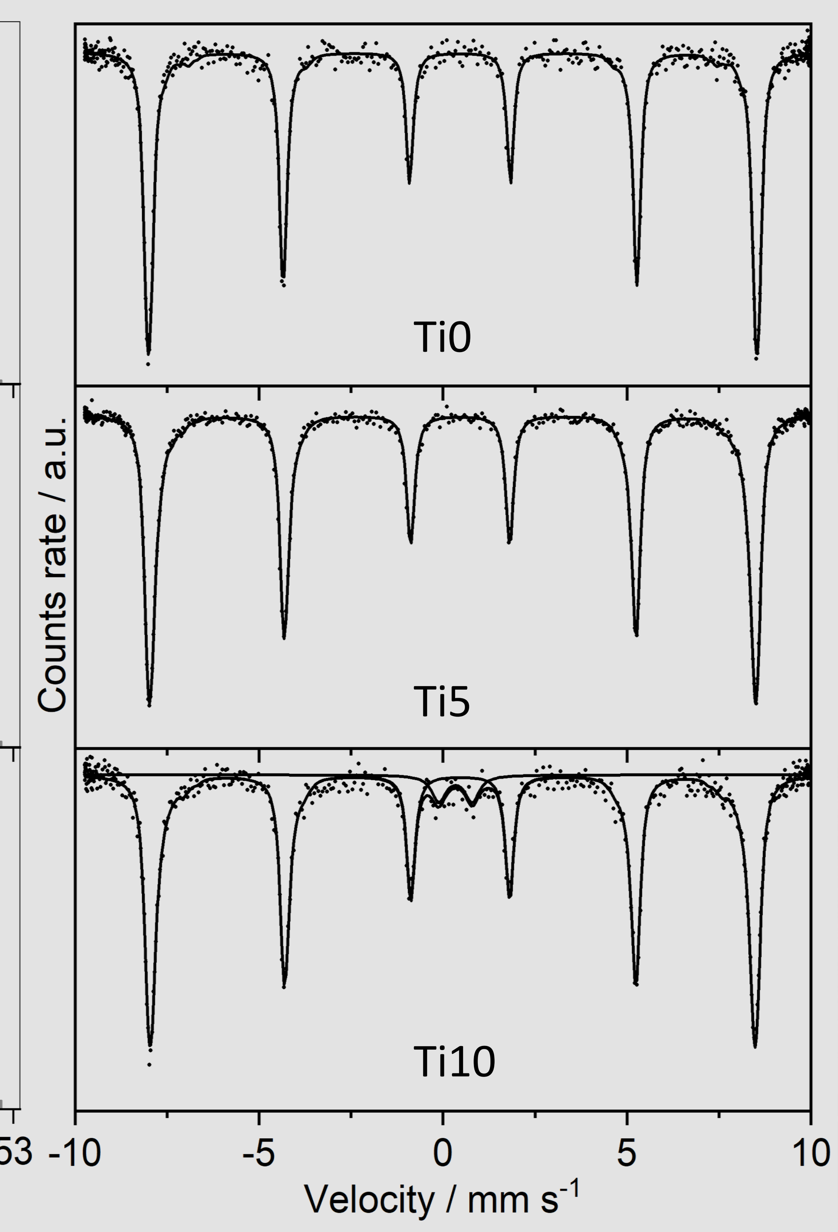


Fig. 3. ^{57}Fe Mössbauer spectra of prepared fibres, recorded at RT. All spectra were fitted using HMF distribution.

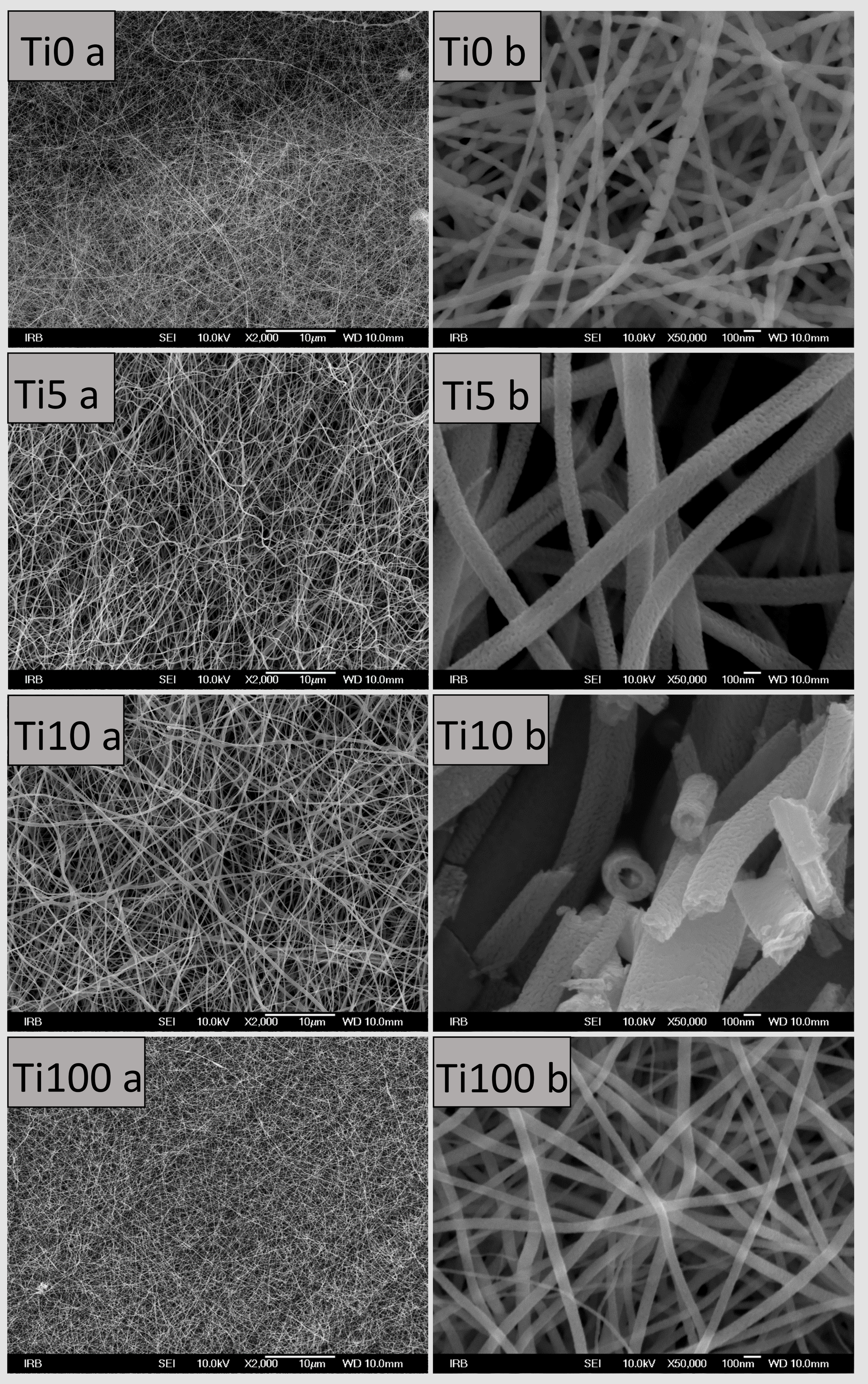


Fig. 4. Low-magnification (a) and high-magnification (b) FE SEM images of the calcined fibres.

Table 1. ^{57}Fe Mössbauer parameters of selected samples recorded at RT.

Sample	Line	δ / mm s^{-1}	Δ or E_q / mm s^{-1}	B_{hf} / T	Γ / mm s^{-1}	Area /%
Ti0	*M*	0.36	-0.22	51.0	0.21	100.0
Ti5	*M*	0.36	-0.20	50.8	0.24	100.0
Ti10	*M*	0.36	-0.20	50.6	0.25	94.2
	Q	0.34	0.91	-	0.45	5.8

Key: δ=isomeric shift relative to α-Fe at RT, B_{hf} = hyperfine magnetic field, Δ or E_q=quadrupole splitting, Γ=linewidth, *M*=sextet, *Q*=quadrupole doublet
Errors: δ and E_q or Δ = ± 0.01 mm s^{-1}, B_{hf} = ± 0.2 T

Table 2. Unit-cell parameters of prepared samples calculated by program Match!

Sample	*a* / Å	*c* / Å	V / Å³	Crystallite size / Å
Ti0	5.0361	13.756	302.16	1067
Ti5	5.0327	13.751	301.65	439
Ti10	5.0306	13.750	301.37	359

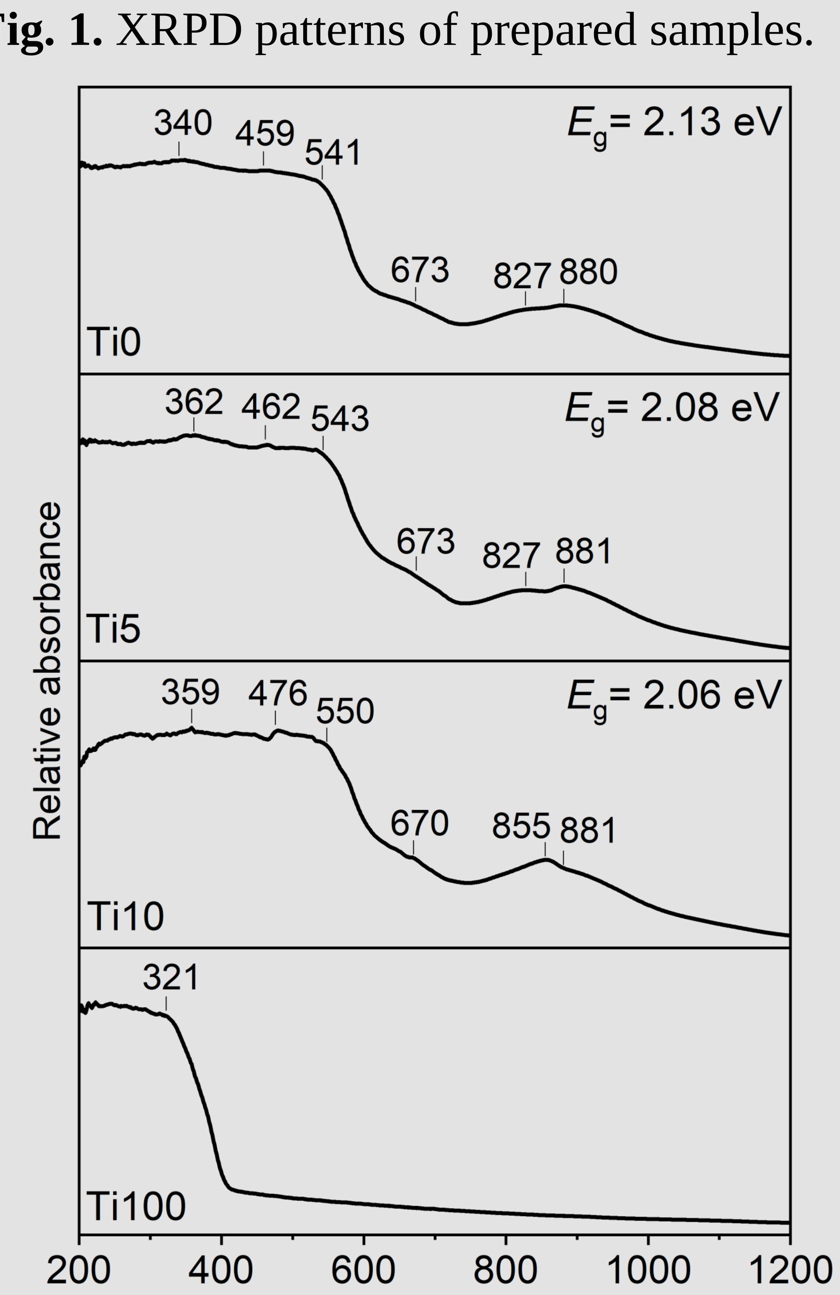


Fig. 5. UV/Vis/NIR spectra of prepared samples.

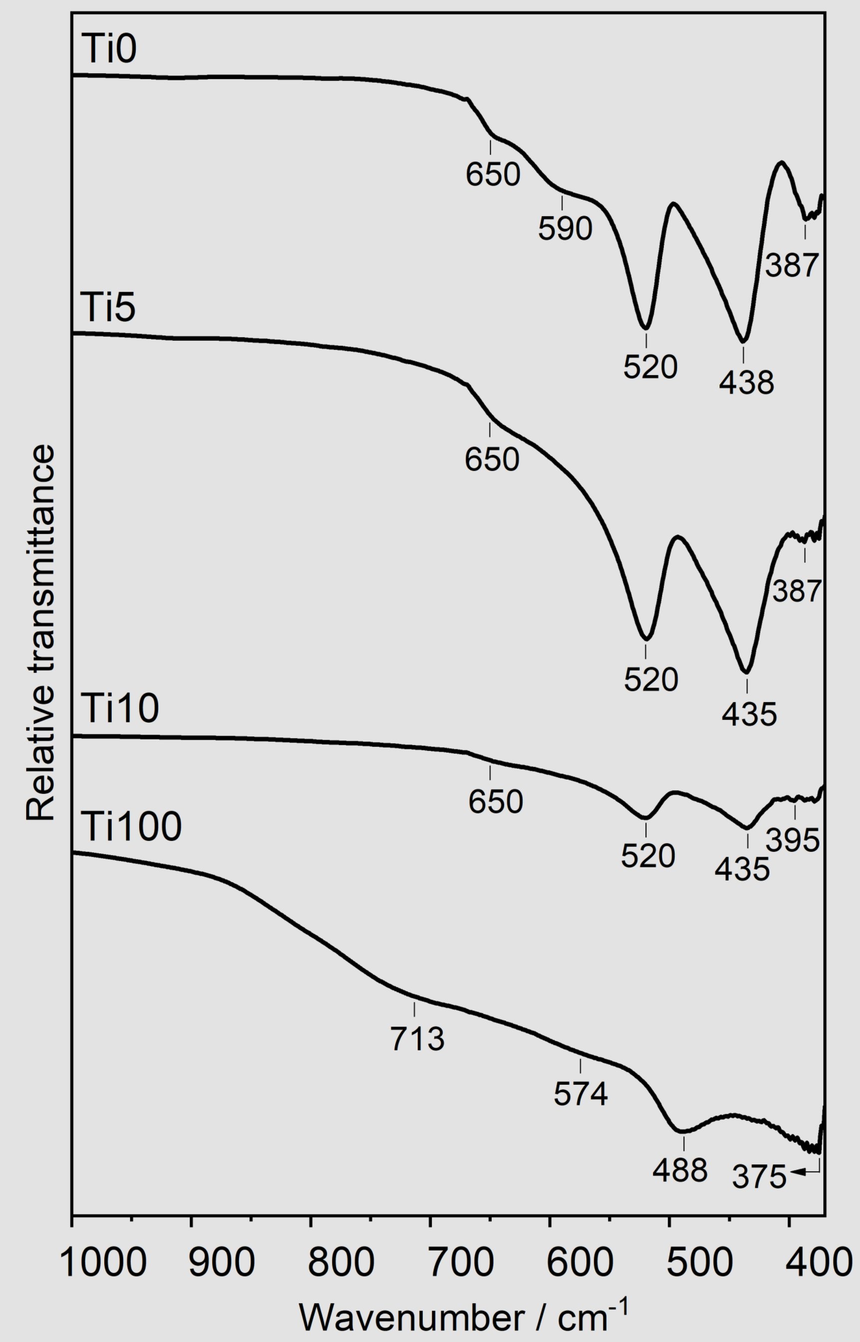
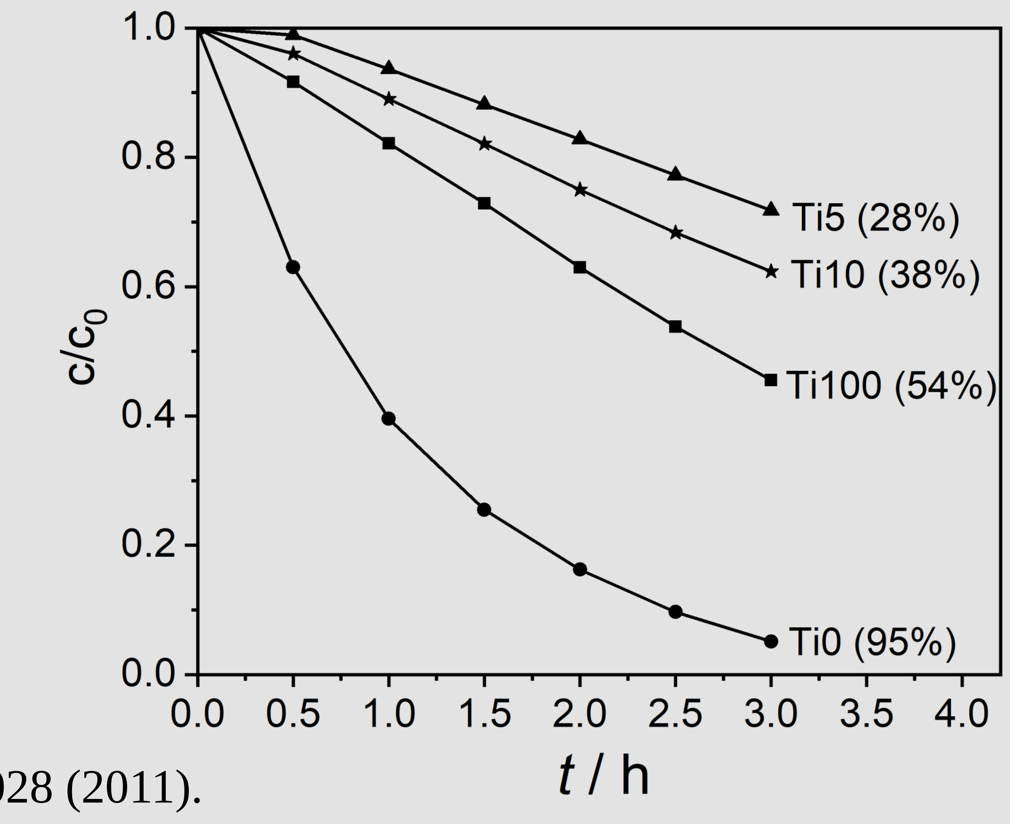


Fig. 6. FT-IR spectra of prepared samples.

Fig. 7. (right) Photocatalytic efficacy of prepared samples. The experiment was carried out with illumination in the visible light range (420 nm < λ < 700 nm).



Conclusions

- Electrospinning method was used to obtain Ti-doped hematite fibres. Hematite and TiO_2 fibres were made for comparison as reference samples.
- Incorporation of titanium cations influenced hematite properties:

1) Crystallinity-Ti-doped hematites are less crystalline. Mentioned samples showed broadening of XRPD lines.
2) Lattice parameters-Ti-doped hematite showed decrease in unit-cell parameters compared to reference sample (Ti0)
3) Magnetic properties-hyperfine magnetic field decreased as a result of Ti-doping
4) Optical properties-maximum at 855 nm is more pronounced in Ti-doped samples and band gap (E_g) decreased
5) Photocatalytic properties-it is shown that Ti10 shows better photocatalytic efficacy than Ti5

References

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