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Preparation and characterization of nanostructured Fe-TiO_2 thin films produced by electrophoretic deposition

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Abstract. Fe-TiO_2 thin films have been produced by a sol-electrophoretic deposition method on metallic Ti foil substrates. X-ray diffractograms and Raman spectra confirms the anatase structure of deposited and annealed Fe-TiO_2 films. Obtained Fe-TiO_2 thin films demonstrate photoactivity under visible light radiation due to the doping with Fe^{3+} ions. Open circuit potential results shows that increase of the film thickness and surface area improves the photoactivity of Fe-TiO_2.

1. Introduction

In recent years nanostructured titanium dioxide (TiO_2) thin films have been focused great interest due to its unique optical and electrical properties, as well as low cost, durability and chemical inertness. TiO_2 thin films have a wide range of practical applications, such as photocatalysts, solar cells, optical filters, antireflective coatings, planar wave-guides and gas sensors. The wide band gap (E_g = 3.21 eV for anatase and E_g = 3.00 eV for rutile [1]) limits application of TiO_2 only in UV irradiation therefore modifications are necessary in order to gain photoactivity in visible light region of the spectrum (~ 40 % of solar radiation). Generally accepted way of extending the spectral response of TiO_2 to the visible light is doping with transition metal ions like Mn(II), Cu(II), Cr(II), Fe(III), Cr (III), V(V), Mo(V) [2, 3, 4].

In this case Fe^{3+} (0.64 Å) is a favorable choice since its radius is close to that of Ti^{4+} (0.68 Å). Furthermore iron ions act like hole-electron pair traps and reduce their recombination rate because the energy level of Fe^{2+}/Fe^{3+} is close to that of Ti^{3+}/Ti^{4+} [5]. The content of Fe^{3+} ions in TiO_2 for optimal photoactivity has been a subject of discussion for some time, however some studies find that 0,1 mol% increases photocatalytic properties most significantly [6, 7].

Photoactivity of the doped TiO_2 substantially depends on the dopant ion and its concentration, as well as preparation method and treatment. Electrophoretic method has been widely applied to obtain TiO_2 thin films [8]. Advantages of electrophoresis over other coating methods are the homogenity of thin films on large substrates, as well as better control of particle size and shape.

The purpose of current work was to electrophoreticaly obtain Fe-TiO_2 thin films that have enhanced photoactivity in visible light. Characterization of these films include determination of TiO_2 phase and particle size (X-Ray diffraction, Raman spectroscopy), as well as surface morphology and microstructure analysis (SEM). To ensure Fe^{3+} content in thin films X-ray fluorescence spectrometry was used. The thickness of films was measured with profilometer.

2. Experimental

The first part of this work includes preparation of Fe-TiO_2 sol. Titanium tetraisopropoxide (TTIP, Aldrich, >97% purity) mixture with isopropanol was hydrolyzed in distilled water, followed by vigorous stirring that lead to peptization. Nitric acid (Lachner, 65%) was used as a catalyst for TiO_2 dispersion in media and Fe^{3+} ions were introduced with iron(III) nitrate nonahydrate (Sigma-Aldrich, >98% purity).

To produce an electrophoretic growth, Pt and Ti electrodes are placed parallel in Fe-TiO_2 sol with a distance 1 cm in between. A constant voltage of -20 V was applied by a DC System Power Supply Agilent Technologies N5751a between the electrodes and held for 1 – 4 min. The as-deposited thin films were first dried at 100 °C for 24 h and then annealed at 500 °C for 2 h.

The morphology of TiO2 films was characterized by scanning electron microscope FEI SEM "Quanta 200". The X-ray diffraction patterns (XRD) were recorded on a Philips X'Pert Pro MPD and Raman spectra by using spectrometer Spex Ramalog. Thickness of Fe-TiO_2 thin films was measured with Veeco Dektak-8 Stylus.

Measurements of photoactivity were carried out in two electrode cell with 0.1 M NaOH water solution as an electrolyte and Pt foil as reference electrode and counter electrode. The samples were exposed to light source (120 W mercury lamp) placed in distance of 25 cm from quartz window of cell. A filter BS3 was used in order to measure open-circuit potential only in visible light. The open-circuit voltage and photocurrent density were measured by potentiostat EG&G PAR Model 173.

3. Results and Discussion

The X-ray diffraction pattern is shown in Figure 1. Diffraction peaks at 25.3° 2θ and 36.9° 2θ are characteristic for anatase phase (average crystalline size 50 – 60 nm). However X-ray diffractogram also shows less intense lines that represents rutile phase at 27.5 ° 2θ and 36.1° 2θ. It is well known, that the mixture of both forms performs with higher photoactivity than pure anatase phase [8].
Figure 2 shows the Raman spectrum of annealed TiO_2 thin films. The bands at 150 cm^{-1} (E_g), 400 cm^{-1} (B_{1g}), 515 cm^{-1} (A_{1g}) and 633 cm^{-1} (E_g) confirm phase transition of electrophoreticaly as-deposited TiO_2 to anatase phase.

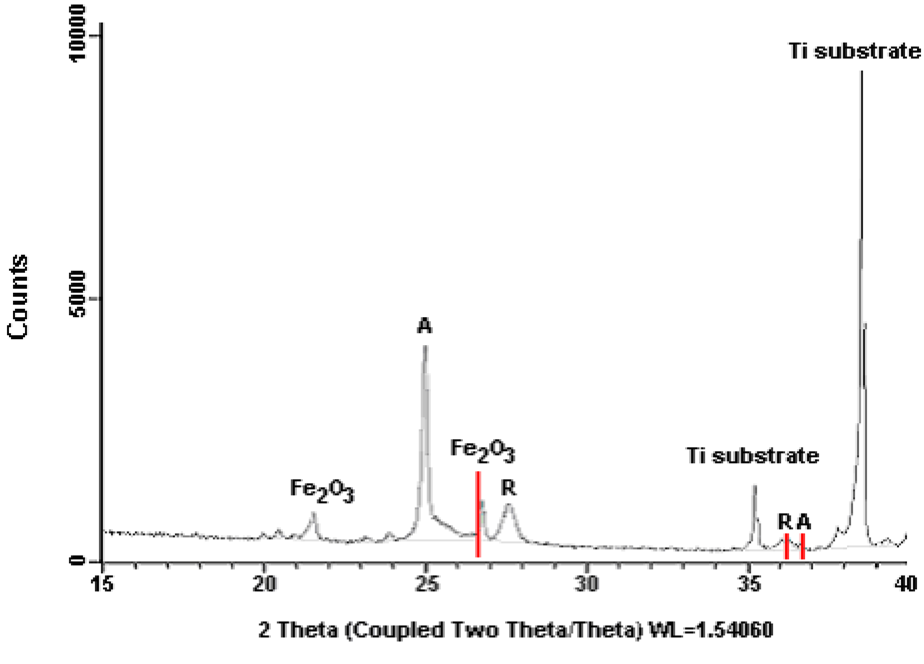

Figure 1. X-ray diffraction pattern of annealed TiO_2 thin film (EPD time –3 min) on Ti substrate (A – anatase, R- rutile)

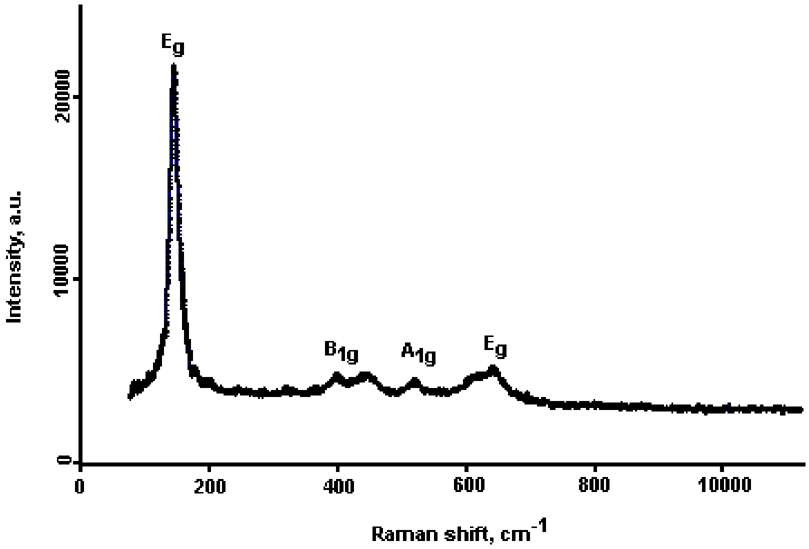

Figure 2. Raman spectrum of annealed TiO_2 thin film (EPD time –3 min) on Ti substrate.

Figure 3 shows the typical SEM images of TiO_2 thin films obtained after 1 min (A), 2 min (B) and 4 min (C) of electrophoresis.

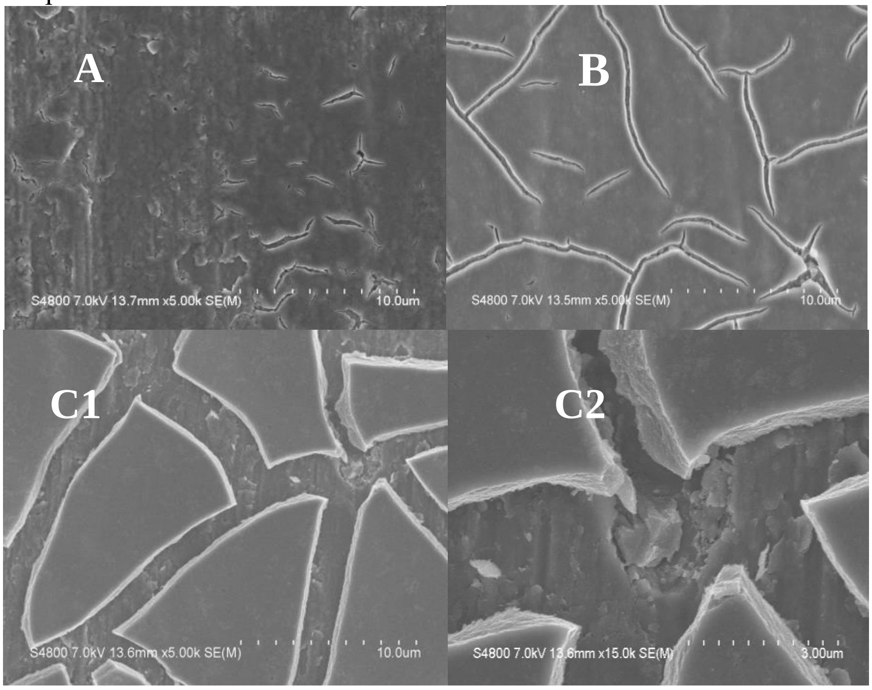

Figure 3. SEM images TiO_2 thin films annealed at 500 °C for 2 h. EFD 1 min (A), 2 min(B) and 3 min (C1 and C2).

Image A of thin film with average thickness of 1.9 μm shows a homogeneous layer of Fe-TiO_2 without significant defects. With the increase of deposition time the following samples seen in images B (3.5 μm) and C (8.1 μm) have developed cracks in thermal treatment that become wider with the increase of thin film thickness. The microstructure of cracks shown in image C2, confirms that the lower part of these cracks is just a deeper layer of Fe-TiO_2 and the splitting has not exposed Ti substrate.

Photoactivity expressed through open circuit potential changes is shown in Figure 4. The Fe-TiO_2 thin film obtained by 4 min electrophoretic deposition (EFD) exhibits the highest potential change both under the UV-VIS and VIS light radiation (0.065 V and 0.040 V, respectively). The same behavior was observed for thin films obtained by 3 min EFD (0.040 V and 0.030 V) and 2 min EFD (0.037 V and 0.030 V). The least activity both in UV-VIS and visible light was shown by Fe-TiO_2 film obtained by 1 min electrophoresis (0.025 V and 0.014 V, respectively). The measured current densities for all obtained thin films were in the range of 0.1 - 1 μA/cm^2.

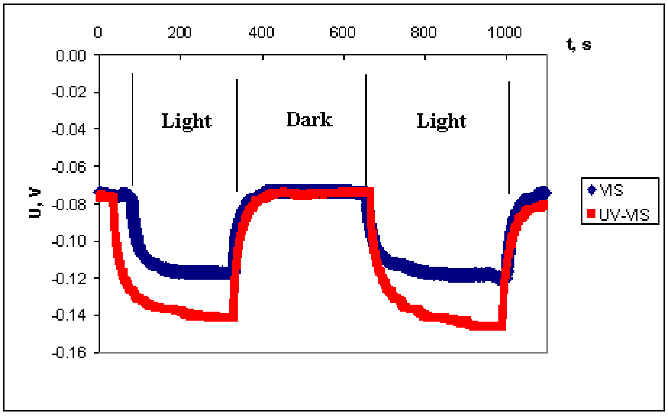

Figure 4. Open circuit potential change for Fe-TiO_2 film obtained by 4 min of electrophoresis.

The distinction of OCP results leads to conclude that active surface area of TiO_2 thin films has been expanded by increasing of the film thickness and surface cracking. Contrary, thinner and more homogenous Fe-TiO_2 thin films exhibit less photoactivity as it is shown for sample A (Fig 3).

Conclusions

In summary, photoactive Fe-TiO_2 thin films have been successfully obtained by a sol-electrophoretic deposition method on Ti substrate. XRD and Raman spectra confirmed that the crystallization of Fe-TiO_2 thin films annealed at 500 °C occurred mainly in the form of anatase phase. Obtained thin films demonstrate photoactivity under visible light radiation due to the doping with Fe^{3+} ions. Thickness and morphology of the Fe-TiO_2 thin films substantially have impact on their photoactivity. Increasing of the film thickness and surface area improves the photoactivity of Fe-TiO_2.

Acknowledgments

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