Ti-doping of hematite films with multilayered particle size distribution by magnetron sputtering

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Abstract. α-Fe₂O₃ films with a layered distribution of nano and submicron particles were synthesized and Ti-doped successfully. Morphology, element and phase composition, electrochemical properties of one-layered, multilayered, and Ti-doped films were investigated. Doped multilayered hematite films have higher catalytic water oxidation efficiency than both undoped films.

1. Introduction
The development of a highly efficient photocatalyst is critical to achieving industrial-scale production of green hydrogen by photoelectrolysis. Hematite, due to its main characteristics, is one of the materials for creating photoanodes for the conversion of solar into chemical energy [1]. One of the ways to increase the efficiency of Fe₂O₃-based photoanodes is to modify photoanodes with various elements, including titanium [2]. Among the doping methods, one of the most promising is a surface modification by physical vapor deposition [3]. In this work, we study the electrochemical properties of films based on titanium modified Fe₂O₃ by magnetron sputtering.

2. Synthesis and characterization of α-Fe₂O₃ powders
Films were obtained by spin-coating at a substrate rotation speed of 400 rpm for 30 seconds. Conductive FTO glasses were used as substrates; the suspension applied to the glass had two different compositions. For series 1, distilled water (10 ml); isopropyl alcohol (10 ml); Fe(NO₃)₃ (5 g); polyethylene glycol (4 g). For series 2, hollow Fe₂O₃ submicron spheres (2 g) were added to the suspension. Films of both series were annealed at 400 °C in an air atmosphere for 4 hours.

Films of series 2 were modified by magnetron sputtering at the following parameters: current of 2.5 A; bias potential of 100 V in an Ar atmosphere (pressure 8·10⁻² Pa) at a substrate temperature of 350 °C (hereinafter, series 3). Titanium was used as the sputter target.

The morphology and elemental composition were investigated by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX), respectively (Vega Tescan 3). The phase composition of the obtained samples was determined by XRD technique on Difrey-401 under Cr radiation. The electrochemical properties of the films were studied by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) in a water solution of KOH 0.1M (P-45X with an FRA-24M electrochemical impedance measurement module). Silver chloride electrode was used as reference. CV setup parameters were as follows: scan rate – 25 mV/s, potential range: from 0 to 1.5 V; number of cycles – 10. Initial parameters for EIS were selected as a constant potential 1 V; applied
potential difference 10 mV. The EIS Spectrum Analyzer software was used to construct an equivalent electrical circuit and fitting the experimental data [4].

3. Results and discussion
The film thickness of series 1 was 0.6 µm (figure 1a); series 2 and 3 were 2 µm (figure 1b). The surface of films of series 1 (figure 1c) is characterized by a porous structure with an average pore size of about 30 nm and an average particle size of about 15 nm. Films of series 2 and 3 have a similar morphology: hollow submicron spheres with an average size of 971 nm are observed on the surface, which is fixed on a layer consisting of nanosized Fe₂O₃ particles. Element mapping of the surface of series 3 film showed that Ti is uniformly distributed (figure 2a); however, dark and light areas indicate phase nonuniformity of the modified films (figure 2b).

The element composition of films of series 1 and 2 is close to the stoichiometric Fe₂O₃ (Fe – 37% (at.) O – 63% (at.)). After modification 26% (at.) Ti was found. These data are correlated with XRD. The Ti-doped hematite films contain TiO₂ and Fe₂TiO₄ (figure 3). Titanomagnetite is a spinel in the FeO – TiO₂ – Fe₂O₃ system. The formation of the spinel is possible because of the interaction of TiO₂, Fe₃O₄ and Fe at temperatures above 300 ºC [5]. Probably, the process of the formation of this phase is associated with the reduction of Fe₂O₃ by the atomic flow of Ti with the subsequent reaction of the formed oxides of iron and titanium.

According to CV tests, the obtained films are stable in an alkaline medium in the potential range from 0 to 1.5 V (vs SSCE). The Bode diagrams (figure 4) show two relaxation times characteristic of semiconductor films. For the fitting, a simplified typical for the process of oxidation of an aqueous solution equivalent circuit was chosen. This scheme model charge transfer from the valence band of a semiconductor to solution [6]. In the selected model, the capacitor was replaced with a CPE element. The replacement of the element is due to the high porosity of the obtained films and their phase inhomogeneity. The results of the approximation are shown in Table 1. In the chosen scheme, R_{ct,bulk} and R_{trap} simulate the recombination centers that reduce the rate of the water oxidation process as recombination of charge carriers in the bulk of the film and on the surface, respectively. The data obtained suggest that series 3 films have a higher efficiency of conversion of sunlight into chemical energy, since they demonstrate lower values of R_{ct,bulk} and R_{trap}.
Figure 3. X-ray diffraction patterns of received films.

Figure 4. Bode diagrams of obtained films.

Table 1. Equivalent circuit parameters.

| Series | $R_s$, Ohm | $R_{ct,bulk}$, Ohm | CPE-$T_{bulk}$ | CPE-$P_{bulk}$ | CPE-$T_{trap}$ | CPE-$P_{trap}$ |
|--------|------------|------------------|----------------|----------------|----------------|----------------|
| 1      | 50         | 76               | $6 \cdot 10^{-5}$ | 0.6            | $8 \cdot 10^{-4}$ | 0.8            |
| 2      | 1          | 75               | $3 \cdot 10^{-7}$ | 0.8            | $3 \cdot 10^{-4}$ | 0.5            |
| 3      | 29         | 63               | $7 \cdot 10^{-3}$ | 0.4            | $3 \cdot 10^{-2}$ | 0.8            |

4. Conclusions

In conclusion, the magnetron deposition method makes it possible to modify Fe$_2$O$_3$-based films with a different-level distribution of powder dispersion with titanium and obtain coatings of the Fe$_2$O$_3$-Fe$_2$TiO$_4$-TiO$_2$ phase composition, in which the water oxidation process is more efficient in comparison with unmodified films, due to a decrease in the concentration of recombination centers in bulk and on the surface of the film.

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